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The Influence of Metabolic Sulphuric Acid Solution on Cement Mortars (CEM II) Modified with Nano-TiO₂

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Abstract. Cement with the addition of TiO₂ nanoparticles is a modern material. It allows ecological use of concrete by making concrete surfaces that demonstrate the ability to reduce airborne contaminants and self-cleaning. This is the result of introducing into its composition nanoparticles titanium dioxide TiO₂, which has photocatalytic properties. Corrosion of concrete in wastewater treatment plants and sewage networks is a serious problem and poses a great threat. The phenomenon of corrosion caused by sulphur bacteria *Thiobacillus* is associated with the formation of biogenic sulphuric acid (VI). Therefore, the tested materials have been subjected to the environment stimulating sulphur bacteria. Used 1.5 mmol/L sulphuric acid solution. Despite the very good properties of mortars/concretes with nano-addition of titanium dioxide and the possibility of their use in various objects, it seems impossible to use sewage treatment plants in tanks. This is related to the deactivation of titanium dioxide after some time.

1. Introduction

The problem of corrosion caused by the presence of sulphur bacteria is common and occurs mainly at sewage treatment plants and in sewerage networks. This process is most intensive in poorly ventilated sewers where sewage is in a concentrated form. Losses caused by sulphate corrosion are considerable and the ways of preventing them are costly [1,2,3].

Cement with an addition of TiO₂ nanoparticles is a modern material that enables ecological application of concrete by producing concrete surfaces [4] displaying capacities of reducing air pollution and self-cleaning [5,6]. This results from the introduction of titanium dioxide TiO₂ particles, which have such properties, into its composition. The nano additive gives it the capacity to reduce harmful nitrogen oxides NOₓ and sulphur oxides SOₓ [7,8] due to the photocatalytic properties of titanium dioxide nanoparticles. Additionally, concrete surfaces made from this material have the capacity of self-cleaning. In order for the above-mentioned qualities to be activated, only a source of energy is required. Light with wavelengths below 410 nm causes displacement of electrons from the valence shell to the conduction band in nanoparticles of titanium dioxide [9]. As a result, electrons (e⁻) are formed on the surface of TiO₂ and then join up with oxygen from the air to form active oxygen (O₂⁻). Also electron holes (h⁺) are formed and these join up with water vapour from the ambient air or with water from atmospheric precipitation and form hydroxyl radicals (OH⁻) which have strong oxidising properties. Active oxygen (O₂⁻) triggers reduction reactions [10]. In effect, the natural process of oxidation is accelerated and thus the disintegration of the harmful substances contained in the air encompassing the structure is also accelerated [11]. Accordingly, the natural process of oxidation is accelerated, which process enhances rapid disintegration of harmful compounds that are
found in the air surrounding the construction structure and contaminating the surface of the plastic or mineral material. Being a photocatalyst, the nano additive is virtually not consumed in the course of the reactions taking place. Theoretically, it can be assumed that these processes are long-lasting and constantly renewable [12,13]. Activation time of a nano additive is typically approximately several tens of hours. After the activation period is over, the process of photocatalysis can take place at night because the energy that is accumulated during the day is then released at night. This process can take place also in the absence of direct sunshine and in cloudy weather because the UV radiation penetrates the clouds but it is then somewhat weakened [14].

CEM II cements are characterised by higher resistance to chemical aggression. This is mainly due to the change in the microstructure of the hardened cement mortar resulting from the pozzolanic and/or hydraulic activity of the mineral additive as well as the extra sealing of the structure with grains of the mineral additive [15].

The objective of the study was an attempt at using the CEM II/A-S 42.5 R cement with a nano-TiO₂ additive at a sewage treatment plant.

2. Corrosive environment and diagnostic features
Changes in the properties of the mortars were evaluated after 3 months of storing samples in an environment of sulphuric acid solution and the same time of storing in moist conditions at the laboratory.

The following changes were selected as diagnostic features that enable evaluation of the impact of the imitated environment of bacterial metabolites on CEM II cement material modified with a nano additive:

- mass moisture content, determined in accordance with PN-EN ISO 12570:2002 [16];
- absorptiveness – determined in accordance with PN-85/B-04500 [17];
- pH value, determined by leaching where a sample with a mass of 10 g was collected and placed in 100 mL distilled water (1:10 ratio). The suspension was mixed several times over 24 hours. Then the suspension was filtered and its pH was determined using an EUTECH CyberComm 6000 ionometer with a glass electrode affixed to it.
- flexural strength was evaluated in accordance with PN-EN 1015-11:2001/A1:2007 [18].

3. The method of preparing materials
The samples used for the tests were made with CEM II/A-S 42.5 R and CEM II/A-S 42.5 R modified with a TiO₂ additive (a commercially available product) in the form of bars with dimensions of 20x20x160mm. In order to make them, standard mortar was used according to the following proportions: 1 portion of cement, 3 portions of standard sand and half a portion of water (W/C=0.5). Therefore, each mixture consisted of 450g cement, 1350g standard sand acc. to PN-EN 196-1:2006 and 225g water. The bars were demoulded after 7 days. Then, they matured for 28 days protected with a film and placed horizontally. After this time, specimens with the nano-TiO₂ additive were exposed to sunshine for 100h on order for the activation of the additive to take place.

In the first stage of the investigation, determination of mechanical and physical characteristics was performed on matured cement bars and the results served as reference values. In the second stage, specimens of the cement-based materials were exposed to the action of sulphur bacteria. This action was imitated by means of 1.5 mmol/L sulphuric acid solution [19]. The pH value of this solution was 2.5. The acid solution was replaced every 1 week for 3 months. This imitated a regular flow of wastewater. After this period, evaluation of physical and mechanical properties was performed.

4. Results and discussions
Results of the investigation into the effect of sulphuric acid solution on the test materials after 3 months of contamination have been shown in graphs in Figures 1 to 4. The graphs contain average values of results from 3 determinations. Dispersion of the results presented did not exceed 0.1%.
Determination of moisture content in the air-dry state of the matured bars showed that the specimens made with standard CEM II cement had slightly higher moisture content than the specimens made with cement modified with the nano-TiO$_2$ additive. Moisture contents for both specimens, made with CEM II modified and unmodified with TiO$_2$ are similar. However, after the 3-month period of exposure they are reduced to 3.1 %mass and 2.6 %mass respectively. Changes in moisture content have been presented in Figure 1.

This can be caused by the reaction between the surface layer of the specimen with the sulphuric acid solution, which resulted in formation of a several millimetre-thick crust.

![Figure 1](image1.png)

\textbf{Figure 1.} The dependence of humidity (moisture content) on time for unmodified and modified TiO$_2$ samples.

Determination of absorbability of the matured cement bars showed that the specimens made with standard CEM II cement has the same absorbability as the specimens made with cement modified with the nano-TiO$_2$ additive. The results of absorbability tests of corroded materials in the air-dry state showed that materials made with cement modified with the nano-TiO$_2$ additive had a higher value of absorbability than the specimens made of standard CEM II cement. The results that were obtained showed that the absorbability values for the corroded specimens were in both case higher than the absorbability values for the uncorroded specimens, which can be seen in Figure 2.

Initial absorbability is virtually the same for both kinds of materials. However, following a period of exposure to the action of a corrosive environment it is increases by 17% for the material made with CEM II without an additive and by 49% for the material made with CEM II with added nano-TiO$_2$.

![Figure 2](image2.png)

\textbf{Figure 2.} The dependence of absorbability on time for unmodified and modified TiO$_2$ samples.

In the course of the investigation, the crust layer present on the surface of the cement bars cracked.
Figure 3. The dependence of pH on time for unmodified and modified TiO$_2$ samples.

An analysis of the pH determination results for the aqueous extracts from the reference materials showed that the pH values for the both kinds of specimens were identical. The pH value of the water solutions of the initial test specimens was 12.4. Changes in pH value have been presented in Figure 3.

Determination of pH values of the aqueous extracts from the corroded specimens showed that the pH value for the specimen made with cement modified with the nano-TiO$_2$ additive is lower than the pH value for the specimens made with standard CEM II cement. The values obtained are lower than in the case of uncorroded cement specimens. After 3 months of exposure to the sulphuric acid solution the pH value was reduced to 11.85 for the unmodified material and to 11.66 for the materials with the nano-TiO$_2$ additive.

Figure 4. The dependence of flexural strength on time for unmodified and modified TiO$_2$ samples.

Results of the determination of flexural strength showed that the specimens made with cement modified with the nano-TiO$_2$ additive had higher flexural strength than the specimens made with standard CEM II cement (Figure 4). The unmodified specimens displayed flexural strength lower by 13% than the ones modified with TiO$_2$.

Determination of flexural strength of the corroded cement bars measured taking into account the outer crust demonstrated that the specimens made with cement modified with the nano-TiO$_2$ additive had slightly higher flexural strength than the specimens made with standard CEM II cement and that the value were in both cases lower than for the uncorroded bars. After the period of three months the strength of both kinds of materials was reduced due to the effect of the corrosive environment. For the specimens made with unmodified CEM II it was reduced by approx. 20% while for CEM II with the additive by approx. 26%.
Figure 5. Photographs of samples from CEM II after treatment with a sulphuric acid solution with a concentration of 1.5mmol / dm³: a) unmodified; b) modified nano-TiO₂.

Due to the action of the corrosive environment in the form of a sulphuric acid solution the cross-section of the specimens was reduced by approx. 4mm concerning the width (b) of the specimen and by 0.2mm concerning the height (Figure 5). The standard samples had an average cross-sectional dimension of approximately 21.7x20.5mm. The specimens were destroyed to the largest extent with respect to the width. The thickness of the specimens was only slightly reduced. Therefore, after the process of corrosion the cross-section dimensions are similar to those of a rectangle. An outer layer (crust), approx. 2-3mm, quite porous, formed on the surface of the specimens. At the contact between the unaffected core and the outer layer formed as the result of the reaction of the material with the corrosive environment there appeared brown spots. They are considerably better visible on the material modified with the nano additive.

5. Conclusions
At present, materials with nano additives or admixtures are taking the world by storm. They are becoming popular thanks to their new or improved qualities. These products are more and more commonly utilised in order to maintain the cleanliness, durability and aesthetics of surfaces and materials, as well as the purity of the ambient air.

The investigation carried out, concerning the effect of bacteria on cement materials, unmodified and modified with a nano-TiO₂ additive has showed that despite very good properties of the CEM II/A-S 42.5 R mortars with a nano titanium dioxide additive and their potential applications in facilities such as tanks at sewage treatment plants or pipes carrying away sewage, materials made with this cement cannot be used. The is due to the deactivation of nano titanium dioxide after a certain time of operation and due to sulphate corrosion caused by the action of metabolites of sulphur bacteria imitated by sulphuric acid solution. It is advisable to investigate application of nano-TiO₂ with other CEM II cements.

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