Application of TiO$_2$ additive to concrete for pyrene degradation. Compressive strength of photocatalytic concrete

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Abstract. In this work, samples of fine-grained concrete were made with the addition of TiO$_2$ powder in a range of 1-3 wt% relative to the cement. The photocatalytic properties of photocatalytic concrete for the degradation of pyrene in solutions of sodium dioctyl sulfosuccinate under UV irradiation were investigated. To evaluate the efficiency of photodegradation, the method of luminescence analysis was used. It was found that the degree of degradation of pyrene in solutions using photocatalytic concrete reaches 25% after 120 minutes under UV irradiation. The compressive strength of the manufactured samples was also studied. A decrease in strength of no more than 24% was registered. To prevent the negative effect of the TiO$_2$ additive, a plasticizer was used. In this case, the compressive strength increased from 19 to 31% relative to the samples without plasticizer.

1. Introduction

Pyrene is a substance from the group of polycyclic aromatic hydrocarbons (PAHs). Substances in this class are found everywhere and are dangerous environmental pollutants [1]. Representatives of PAHs possess carcinogenic and mutagenic properties, many of them are very dangerous for human health and can provoke the development of oncological diseases [2]. In most cases, PAHs are formed as a result of pyrolysis of organic fuels. Currently, in many large cities, the PAHs content exceeds the MPCs, which is largely due to the steadily increasing anthropogenic impact on the environment. In this regard, the development of methods for reducing PAHs concentrations to improve the state of the environment is an urgent task.

One of the prospective ways of degradation of PAHs is the use of building materials with photocatalytic properties. In particular, it is relevant to study photocatalytic concrete (PhC), which are able to decompose ecotoxicants on their surface, thereby reducing their concentration in the air [3]. This process occurs with photocatalytic reactions (photocatalysis) under the influence of light radiation. As a rule, PhC is made according to the production technology of regular concrete, but the photocatalytic additive is introduced into the dry mixture before mixing with water.

Today, one of the most used photocatalytic additives in concrete is titanium dioxide (TiO$_2$) [4]. TiO$_2$ is a widely used photocatalyst due to its high photocatalytic activity, low cost, low toxicity, and good chemical and thermal stability [5]. It is also known that TiO$_2$ significantly accelerates the degradation of PAHs when exposed to artificial or natural light [6]. For example, in [7] it was proved that the degradation of pyrene by TiO$_2$ proceeds with the formation of relatively safe intermediate products of the reactions. As a result of the study, it was found that PAHs molecules can be mineralized to CO$_2$ and H$_2$O.
To determine the substances of the PAH group, it is effective to use the method of luminescent analysis of solutions [8]. This method does not require long-term sample preparation and is highly sensitive. The method of luminescence analysis makes it possible to study the process of photocatalytic degradation of PAHs in solutions. Then, based on the obtained data, it is possible to evaluate the efficiency of using photocatalytic materials.

The purpose of this work is to develop compositions of PhC and to study their effectiveness for the degradation of pyrene under artificial lighting. It is also known [9] that the use of TiO$_2$ as an additive to the concrete can significantly influence the hardening processes of cement stone and lead to changes in the strength characteristics of samples. In this regard, the influence of the photocatalytic additive on the strength characteristics of the manufactured PhC samples was studied.

2. Materials and methods
Samples of fine-grained concrete with dimensions of 2×2×2 cm were made. Then the samples were solidified at a relative humidity of 90-95% and a temperature of 20±2°C. As a binder, Portland cement “Eurotsem 500 Plus”, CEM I 42.5 H produced by LLC “Peterburgcement” was used. Sand with a grain size module of 2.0–2.5 according to State Standard, Russia №8736-2014 was chosen. For preparing the mixture, components were used in the ratios cement/sand=1/3, W/C=1/2. The content of the TiO$_2$ additive (Puriss. spec., Promchim, Russia) in the mixture was remained within a range of 1 to 3 wt% relative to the cement. The average diameter of particles was $d=21±5$ μm.

After the production of concrete samples with the addition of TiO$_2$, the process of photocatalytic degradation of pyrene (Fluka, Germany) was studied in the model media. Pyrene has an electron-vibrational structure of the fluorescence spectra, which is characterized by five well-resolved main vibronic bands. This representative of PAHs does not have a high toxicity, which makes its use in laboratory studies relatively safe [8].

An aqueous solution of anionic surfactant sodium dioctyl sulfosuccinate (DSS) at the concentration of 10$^{-2}$ M was used for the extraction of PAHs. The concentration of the resulting pyrene solution was $C_{pyr}=10^{-4}$ M. Solutions of pyrene and DSS were prepared on distilled water (pH=7.0).

On the 28th day, the prepared samples were kept (Figure 2) in previously prepared pyrene solutions with DSS and irradiated under UV lamp for 120 minutes (Cameleon lamp 26 W, $\lambda=365$-395 nm). Then the obtained solutions were filtered using a filter paper “red ribbon” (State Standard, Russia №12026-76) to remove large particles of concrete. The HORIBA Fluorolog-3 TCSPC modular system was used for luminescent analysis of pyrene solutions after keeping the concrete samples. The error of the measured parameters consisted of the error of the emission monochromator and the error of measuring the luminescence intensity. According to the HORIBA manufacturer the value of the error of the monochromator radiation is 0.5 nm [10].
After studying the photocatalytic properties of the manufactured concretes, the effect of the TiO$_2$ additive on the cement stone hardening processes was studied. The compressive strength was measured using a ToniNorm testing machine (Toni Technik, Germany) on the 1st, 3rd, 7th and 28th days of hardening.

Samples were also made with the plasticizer “Stachement (St.) 1267” based on polycarboxylates (Stachema, Poland) with a fixed amount of 2.7 wt% relative to the cement. The effectiveness of the additive was compared with samples made without the additive (control composition).

3. Results and discussion
In the experiment, the luminescence spectra of pyrene ($\lambda_{ex}$=320 nm) were obtained after keeping of PhC samples in solutions under UV irradiation ($t$=120 min). Then, based on the obtained data, the graphs of pyrene photodegradation were plotted (Figure 3). The graphs make it possible to estimate the efficiency of pyrene oxidation in the process of photocatalytic reactions on the surface of PhC samples, depending on the amount of TiO$_2$ additive. This shows the ratio of the $C_0-C_t$ concentration difference to the $C_0$ concentration. In this case, $C_t$ is the concentration of pyrene in solutions after keeping the PhC samples under UV irradiation for time $t$, $C_0$ is the initial concentration of pyrene in solutions before UV irradiation ($t=0$ min). The graphs show that the pyrene concentration in the solutions after keeping the PhC samples with the addition of 3% TiO$_2$ decreased by 25%. Also the pyrene concentration decreased by 5% for the control sample without the addition of TiO$_2$ after 120 min under UV irradiation.

In general, the results of photocatalytic studies confirm that the addition of TiO$_2$ is effective for the decomposition of pyrene. This proves the feasibility of using PhC in modern environmental conditions. However, in practice, in addition to the photocatalytic properties, PhC must have sufficient physical and mechanical properties, which requires appropriate research.

It is known [11, 12] that in some cases, the addition of TiO$_2$ to the concrete can lead to a decrease in compressive strength. For example, in the study [11], the strength of the PhC with 3% TiO$_2$ samples decreased by 35% compared to the control samples.

The test results of concrete samples with the addition of TiO$_2$ in various concentrations and control samples are shown in Figure 4.

From the obtained values of the strength of concrete samples, it can be concluded that the use of the TiO$_2$ additive leads to a decrease in the compressive strength of concrete by no more than 24% compared to the control samples. Moreover, PhC samples with 3% TiO$_2$ showed the largest decrease in compressive strength on the 28th day. This may be mainly due to a minor increase in the porosity of the concrete and an unequal distribution of TiO$_2$ particles [12]. This effect leads to the formation of TiO$_2$ particle conglomerates and the concentration of stresses in the concrete structure [11].

The negative impact of the TiO$_2$ additive on the properties of the concrete can be minimized by accurately calculating the proportions of the concrete mixture. In turn, the required compressive strength
can be achieved by using a plasticizer. The W/C ratio is also important, according to the authors [12], the optimal W/C ratio is 0.5. In the study [13], it is noted that the addition of plasticizers to PhC can eliminate some significant drawbacks of the samples, such as high porosity and low hydration. Also flowability is improved and cement consumption is reduced.

The results of compressive testing of concrete samples are shown in Figures 4, 5. It was found that the use of a plasticizer significantly increases the strength characteristics of the PhC in comparison with samples without a plasticizer. For example, for PhC samples, the compressive strength on the 28th day increases by 19% with the addition of 1% TiO$_2$, by 30% with 2% TiO$_2$, and by 31% with 3% TiO$_2$. It is also essential to note the increase in the strength of the PhC with the plasticizer in comparison with the
control samples. The largest strength was demonstrated by PhC with 2% TiO$_2$, which exceeded the strength of the control sample by 10% on the 28th day.

Based on the literature data, it can be assumed that the improvement in strength characteristics can be caused by the influence of small amounts of TiO$_2$ additives on the silicate phases of cement, primarily on C$_3$S. For example, the authors [14] found that when adding 3% TiO$_2$, the photocatalyst accelerates hydration and the development of C-S-H phase due to an increase in the amount of Ca(OH)$_2$ at the initial stage of hydration. However, the same research group found that the addition of TiO$_2$ powder in an amount of more than 3% led to a decrease in strength. This was caused by a decrease in the formation of Ca(OH)$_2$ crystals required for the production of C-S-H gel during the hydration process. In addition, the unequal distribution of TiO$_2$ particles in the concrete matrix had a negative effect, which was also noted by the authors [13].

4. Conclusion
The conducted studies showed the efficiency of pyrene degradation on PhC samples under UV irradiation due to the photocatalytic properties of TiO$_2$. In the case of using PhC samples with the addition of 3% TiO$_2$, up to 25% of pyrene was photodegraded under UV irradiation after 120 minutes. At the same time, relatively harmless reaction products enter the environment without a dangerous effect. Thus, the conducted studies have proved the effectiveness of using TiO$_2$ as a photocatalytic additive in concrete for the degradation of some representatives of PAHs.

The strength characteristics of the manufactured PhC samples were also studied. It was found that the compressive strength of the PhC samples decreased by no more than 24% compared to the control samples. To prevent a decrease in strength, samples with the addition of a plasticizer were studied. In this case, the compressive strength of the samples with different TiO$_2$ contents increased from 19 to 31% relative to samples without plasticizer. Also, the obtained strength values exceeded the results of the control sample by 10% on the 28th day of hardening. The addition of TiO$_2$ more than 3 wt% of the cement is inappropriate due to the significant increase in the cost of the mixture and the negative effect of the photocatalytic additive on the physical and mechanical properties of the PhC.

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