Ecological efficiency photocatalytic concrete

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Abstract. The process of urbanization is accompanied by the formation of a high density of street highways, buildings, people, transport and industrial enterprises, high energy consumption, an increase in the amount of waste and the release of a large amount of pollutants into the atmosphere and the aquatic environment. Air pollution is one of the most serious environmental problems in cities and poses a threat to vegetation, animals, materials and human health. One of the main environmental pollutants is nitrogen oxides (NOₓ). Finding ways to remove NOₓ from the surrounding air is a necessity today, as it will help to improve the ecology of large cities, as well as reduce O₃ concentration at ground level. Titanium Dioxide (TiO₂) is a natural semiconductor material that is widely used in many industries. In construction, titanium dioxide is used to create building materials with a self-cleaning surface. In recent years, a fairly powerful photocatalytic effect of surfaces with titanium dioxide has been discovered. Self-cleaning combined with the photocatalytic effect of TiO₂ makes it an ideal additive in the production of building materials for urban environments. Depending on the application, TiO₂ can be used as a coating, additive in concrete, gypsum or paint. TiO₂ can be used for surfaces of paving elements or building facades, retaining walls, tunnels. In this paper, we study the effect of the addition of titanium dioxide on the formation of the physicochemical properties of concrete.

1. Introduction
The first use of concrete with self-cleaning properties dates back to 1996, when Italcementi participated in the construction of the church Dives in Misericordia in Rome (completed in 2003). This project involved the construction of a complex structure of three huge white sails, which are assembled from precast concrete. In such a building, it was required to use concrete, unique in its properties. Concrete of high strength and durability, had to retain white color indefinitely due to the self-cleaning properties of the surface.

It is known that the main reason for staining cement materials, which are a porous body, is the accumulation of colored organic compounds in the surface layers of materials. Cement composites with TiO₂ nanoparticles retain their esthetic characteristics, especially color, for a long time even under the influence of an aggressive urban environment.
After the construction of the church in Rome, photocatalytic concrete was used in other European architectural projects in France, Belgium and Italy. Concrete was also used as a material that controls the ecology and air quality of megacities [1].

Already, Ukraine has faced the problem of controlling air pollution from vehicle emissions, especially in growing urban areas.

The main air pollutant in the city is motor vehicles, and the main danger to humans is traffic fumes. They contain more than 200 chemical compounds.

Harmful ultrafine particles from car exhaust can lead to asthma, allergies, heart disease, lung cancer. According to the World Health Organization, annually about 3 million deaths are due to air pollution, largely due to car exhaust.

New developments in concrete offer the inclusion of photocatalytic TiO$_2$ nanoparticles in concrete, which can reduce environmental air pollution (for example, by decreasing the content of nitrogen oxides when exposed to ultraviolet radiation) and promote self-cleaning of the concrete surface.

As a result of exposure to sunlight, titanium dioxide nanoparticles act as a photocatalyst, which turns water vapor and atmospheric oxygen into atomic oxygen. The active oxygen that is released as a result of this reaction is enough to kill bacteria, oxidize and decompose organic pollutants, and deodorize rooms. Houses made of cement composites with titanium dioxide nanoparticles retain their color for a long time, despite the influence of an aggressive urban environment.

The TiO$_2$ photocatalyst activates ultraviolet (UV) radiation to oxidize air pollutants such as nitrogen oxides (NO$_x$) and volatile organic compounds (VOCs) [2]. The application of the photocatalytic effect of TiO$_2$ on a concrete coating to remove pollutants from the air is a promising alternative for removing pollutants from the street. This article compared various ways of using TiO$_2$ in concrete and evaluated the effectiveness of protective coating materials when removing pollutants from the atmosphere, preserving self-cleaning properties.

2. Architectural shells of glass fiber reinforced concrete

The experience of construction in our country and abroad shows that fiber-reinforced concrete is one of the promising building materials of the 21st century [3]. The study of dispersed reinforced concrete allows the production of lightweight building structures with increased strength.

The use of fiberglass in concrete as a fiber has shown that a strong and relatively light composite with a high fracture toughness and a fairly wide range of applications is obtained. [4].

Glass fiber reinforced concrete combines the positive properties of concrete regarding high compressive strength and, at the same time, thanks to the inclusion of fibreglass, it has increased crack resistance, water resistance, and operational stability.

Fiber concrete, in comparison with concrete of a similar brand, can have a tensile strength at bending higher by 4-5 times, axial tension higher by 3-4 times, impact strength more than 15-20 times, and this is important for the operation of a significant part structural elements.

The main advantages of fiberglass concrete products are their increased decorativeness, architectural expressiveness and plasticity, which can be used to improve the appearance of buildings. All this contributed to an increase in interest in fiberglass concrete and the expansion of its effective use in construction.

The development of the organization of the technology for the manufacture of fiber-reinforced concrete is based largely on basic research. Scientists from Japan, the USA, Norway, Germany, France, Great Britain, and China made a great contribution to the development of various methods for producing fiber-reinforced concrete.

Currently, interest in the study of fiber-reinforced concrete manufacturing technologies among scientists from around the world is due to the need to obtain building materials based on local raw materials with enhanced performance characteristics that provide high energy efficiency, environmental safety and low cost.

This primarily relates to the facades of buildings and constructions that form the outer shell of the building and serves different purposes. The facade protects the interior from environmental conditions
such as wind, rain and sun. Another key aspect of a modern facade cladding is to creation of a unique appearance for the building. A facade system usually consists of the facade cladding, a two-dimensional element that is supported by a primary and/or secondary structure [5]. Various materials for the cladding have been used in architecture ranging from more traditional envelope materials such as glass, metal, stone, timber, concrete, etc. to materials that have been developed during the last decades such as glass fiber reinforced plastic (GRP), glass fiber reinforced concrete (GRC).

The ability to produce thin-walled (1-2 cm thick) glass fiber reinforced concrete shells of almost any shape and configuration provides wide prospects for their application for cladding facades of residential and industrial buildings, as supporting structures or decor elements.

The mechanical strength of glass fiber reinforced concrete is 150% higher than the strength of ordinary, its frost resistance is 50% higher, and the likelihood of cracking is several times lower. It is worth noting that the weight of a structure made of such concrete is reduced several times. Three types of glass fiber reinforced concrete are used in construction: lightweight; medium strength; high strength.

Lightweight glass fiber reinforced concrete is used in the construction of small private houses, utility rooms, to create partitions between rooms and other non-load-bearing structures. Nanostructured lightweight concrete is used in bridge construction.

Glass fiber reinforced concrete of medium strength is used in the construction of buildings, bridges and roadbed.

Glass fiber reinforced concrete of increased strength is used to create load-bearing structures of structures, elevator shafts and where high strength is required. A variety of requirements are imposed on concrete as the main building material in various projects. But almost always the designer is interested in access to structural concrete with a minimum specific gravity, while maintaining or even developing the bearing capacity of parts made of such concrete.

To improve the properties of architectural shells made of glass fiber reinforced concrete and provide them with environmental characteristics, it is proposed to use the addition of titanium dioxide.

Titanium dioxide TiO$_2$ is a natural compound that is used in a variety of applications, from consumer products to architectural coatings. It is also the best semiconductor material for photocatalytic applications [6]. TiO$_2$ occurs in nature as rutile, anatase and brookite. Rutile is the most common and thermodynamically stable form and is mainly used as a colorful pigment. Brookite is rare and has few common commercial uses [7-8]. Anatase is chemically stable at room temperature, non-toxic and economically beneficial as a photocatalyst compared to other semiconducting materials such as zinc oxide (ZnO) [9-10]. The most common, commercially available form of TiO$_2$ for photocatalysis is titanium dioxide with an average primary particle size of 21 nm and an anatase-rutile ratio of 80/20 [11-12]. Many researchers studying photocatalytic materials have used this commercial product for direct testing or for comparison with other semiconducting materials.

3. Photocatalysis in concrete

The photocatalytic properties of titanium dioxide in the anatase phase have been used to create various materials since the mid-1990s [13-14]. At first, titanium dioxide was used as a white pigment in the paint and varnish industry, it allows not only to obtain coatings of various colors, but also significantly improve their properties. Then, self-cleaning phenomena, the so-called “lotus effect” [15], were detected on surfaces treated with titanium dioxide, due to their high hydrophilicity (Fig. 1).

Currently, the possibilities of using titanium dioxide for the decomposition of organic and inorganic substances on the surface of materials, the so-called process of photooxidation [16] (Fig. 2).
Photocatalysis is a process that occurs on the surface of a semiconductor that is exposed to light. When a photon whose energy is equal to or greater than the band gap (3.2 eV для TiO₂) of a semiconductor is absorbed, an electron (e⁻) moves from the valence band to the conduction band. The result is the presence of a “hole” in the valence band (h⁺). H⁺ and e⁻ are strong oxidizing agents and reducing agents, respectively. An electron-hole pairs can react with electron donors or acceptors adsorbed to the surface of a semiconductor. If the reaction does not occur, the pair of electron-hole pairs recombine and the energy dissipates as heat. Oxygen and water adsorbed on a semiconductor surface, catalyzed with the formation of reactive species, superoxide anion O₂⁻ and hydroxyl radical (OH⁻):

\[ h^+ + H_2O \rightarrow OH^- + H^+ \]
\[ e^- + O_2 \rightarrow O_2^- \]

Hydroxyl radicals and superoxide anions are strong oxidizing and reducing agents. They can react with contaminant molecules adsorbed onto a photocatalytic surface, such as NOₓ or hydrocarbons, to form nitric acid, carboxylic acid or carbon dioxide.

Thus, the use of TiO₂ in concrete is aimed at achieving two main effects - self-cleaning from dirt and purification of the atmosphere due to the oxidation of nitrogen oxides (NOₓ) as a result of photocatalysis.

Photocatalytic cement-based materials were used in architectural projects in Germany, Belgium, Italy, Spain, France, and Japan [16-18]. For example, in France, “green technologies” using TiO₂ were used in the construction of the “Porte de Vanves” metro station in Paris. In Japan, photocatalytic surfaces
are used at airports to control harmful substances in the air. For the first time in Italy, photocatalytic coatings were used in the “Via Porpora” tunnel in Milan.

4. Materials and methods
For research, raw materials were used, which are usually used in the manufacture of fiberglass concrete products:

1. Portland cement CEM I 52.5;
2. Sand Мк =1;
3. Alkali-resistant fiberglass with fiber length 12 mm;
4. Chemical additive Sika ViscoCrete-5-600;
5. Titanium dioxide anatase-rutile ratio 80/20.

In laboratory conditions, studies have been carried out of the photocatalytic removal of air pollutants. Most of these studies have focused on the ability of concrete containing TiO₂ to remove one type of pollutant. As a result, the test materials were usually exposed to air containing only one interesting pollutant, rather than a mixture of pollutants similar to that found in urban air. In previous laboratory studies, realistic environmental conditions or air mixtures were rarely used, making it difficult to estimate expected air emissions. However, the previous laboratory test results can be used to better understand the mechanisms leading to the oxidation of NOₓ and other pollutants, and what parameters affect the photocatalytic process.

There is a discrepancy in the literature [2, 8-12] regarding the mechanisms that occur during heterogeneous NOₓ photocatalysis. An understanding of the mechanisms involved in these reactions is necessary in order to correctly describe and evaluate the kinetic parameters that control the reaction process.

It is generally accepted in the literature that ОН⁻ and О₂ are reactive species created on the surface of a photocatalytic material. Two mechanisms are proposed for the destruction of NO, each of which includes one of these reactive species as an initiator of the removal process.

Several researchers [17-18] have proposed a mechanism involving hydroxyl radicals, and this is the most common mechanism in the literature. The proposed mechanism is such

$$\text{NO}_{\text{ads}} + \text{OH}^- \rightarrow \text{HNO}_2$$

$$\text{HNO}_2 + \text{OH}^- \rightarrow \text{NO}_2\text{,ads} + \text{H}_2\text{O}$$

$$\text{NO}_2\text{,ads} + \text{OH}^- \rightarrow \text{HNO}_3$$

Several researchers have studied the effect of irradiation on the photocatalytic activity of TiO₂. The photocatalytic activity of TiO₂ is affected by the intensity and nature of light. Despite the large differences in the experimental conditions used to test photocatalytic materials and the variations of the most tested materials, it is difficult to quantify the results of various studies. However, some qualitative results have been found in various studies [19-20]. The photocatalytic activity of materials containing TiO₂ increases linearly with light intensity at low light intensity until the light intensity reaches about one equivalent of the sun (1 mW cm⁻²).

The activity of air purification with titanium dioxide used in building materials was determined by the oxidation of NO and NO₂ to NO₃. Particular attention is paid to these pollutants, since they are the main components of traffic fumes and play an important role in the formation of smog in large cities.

The experimenta set-up (Fig. 3) consists of a plastic container in which the concrete sample with a TiO₂ coating is located. The container is covered with glass that transmits ultraviolet radiation. Air from an internal combustion engine that contains nitrogen oxides is blown into a container on a concrete surface. Ambient temperature – 23±2 °C and relative humidity – 50%. The light intensity is 10 W/m² with a wavelength in the range 300...460 nm. Concentration is measured at the exit of the container. Measurements are taken at 7:00. At the beginning, the initial concentration of NO and NO₂ in the air of the container is measured. To activate photocatalytic reactions, sunlight or an artificial source of ultraviolet radiation is used.
5. Results and discussion
After reaching the maximum concentration of NOx = 5 g/m³ in the container, the engine turned off. The reading of the gas analyzer was carried out with an interval of 1 hour. The measurement results are shown in Fig. 4.

The nature of the decrease in the concentration of NOx depends on the size of the concrete surface, the initial concentration of NOx, light intensity and ambient temperature. A 6-fold increase in the photocatalytic surface contributes to a decrease in NOx concentration to 82%.

In Fig. 5 shows the effect of the thickness of the TiO₂ layer, which is deposited on concrete samples, on the NOx reduction efficiency. The test was performed at 30% humidity, ultraviolet radiation intensity of 2.4 mW/cm² and low pollutant feed rate of 3 min⁻¹.
As can be seen in fig. 5, an increase in the layer thickness had a positive effect on the NO\textsubscript{x} reduction efficiency, since an increase in the thickness led to an increase in the NO\textsubscript{x} removal efficiency. The results show an average NO\textsubscript{x} reduction efficiency of 34% for a 12.5 mm TiO\textsubscript{2} layer thickness compared to a 62% reduction for a sample with a 75 mm layer thickness. This indicates the possibility of applying a TiO\textsubscript{2} layer on the surface of road surfaces, since UV light can penetrate to a considerable depth, enhancing the photocatalytic efficiency of the sample.

Operational properties were evaluated by standard physical and mechanical studies. The experimental results showed that the addition of TiO\textsubscript{2} to the concrete composition increases the compressive strength of concrete by 5-7%, reduces water absorption by 1%. In addition, the introduction of TiO\textsubscript{2} nanoparticles leads to an increase in the strength of fine-grained concrete: bending after 7 days by 1.8 times, after 28 days by 1.2 times; compression 7 days 1.7 times, and after 28 days 1.5 times.

**Table 1 Compressive strength of concrete after**

| Samples       | Days | Compressive strength, MPa |
|---------------|------|---------------------------|
| Control sample | 7    | 67.5                      |
| TiO\textsubscript{2} sample | 7    | 72                        |
| Control sample | 28   | 74                        |
| TiO\textsubscript{2} sample | 28   | 77.5                      |

The study of the structure of concrete by optical microscopy is shown in Fig. 6. As shown by microscopic studies, the introduction of TiO\textsubscript{2} contributes to the compaction of the concrete structure. The presence of a surface coating from a TiO\textsubscript{2} layer in the form of a white coating is observed (Fig. 6, b).

A study by thermoprometry [19] showed that with the introduction of nanodispersed titanium dioxide additives, the porosity of fine-grained concrete is redistributed in size (Fig. 7) - a decrease in the size and volume of capillary pores and an increase in the fraction of gel pores.
Figure 6. Microscopic examinations: a) control sample; b) TiO$_2$ sample

Figure 7. Microporosity of cement stone: a) pore size distribution; b) pore volume
A sharp decrease in micropore volume is due to a change in the nature of adsorption processes at the solid phase – pore liquid interface and the filling of large pores with particles of titanium dioxide.

Thus, after mixing, TiO₂ very well compacts the structure of cement stone in the same way as silica fume or other fine fillers. In addition, TiO₂ helps to increase erosion resistance and reduce the amount of pollutants that penetrate the pores.

6. Conclusions

The use of titanium dioxide will significantly improve the environmental situation of large cities in terms of cleaning surfaces from dirt and dust and air purification from organic compounds and NOₓ. Titanium dioxide helps to improve the physical and mechanical properties of glass fiber reinforced concrete, densification of its structure. Gives specific properties to its surface, which promotes self-cleaning from dust and dirt. TiO₂ is an effective material for removing NOx pollutants from the air stream when used in the composition of sustainable Fiberglass Concrete with a coefficient of performance from 34% to 62%.

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