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# Concretes with Photocatalytic Activity

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Additional information is available at the end of the chapter

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## Abstract

This chapter is a short review about the modified concretes with photocatalytic activity. In the beginning, the photocatalysis process is explained; the authors are focused on the mechanism of organic contamination and nitrogen oxide decomposition. Next the three main methods for concretes modification are presented: the first group is when the concrete is covered by thin layer of  $\text{TiO}_2$  materials, e.g., paints or  $\text{TiO}_2$  suspensions. The second group is the concretes with thick layer of photoactive concrete on the top. The third group constitutes concretes modified in mass with  $\text{TiO}_2$ . The two main methods for photocatalytic activity of the modified concrete determination were shown: an air purification by a nitrogen oxide decomposition and the self-cleaning properties by dyes decomposition. Also in this chapter the mechanical properties of the modified concrete are presented. In the end, the examples of the buildings made of photocatalytic concretes are shown.

**Keywords:** modified concretes, photocatalysis, air purification, mechanical properties

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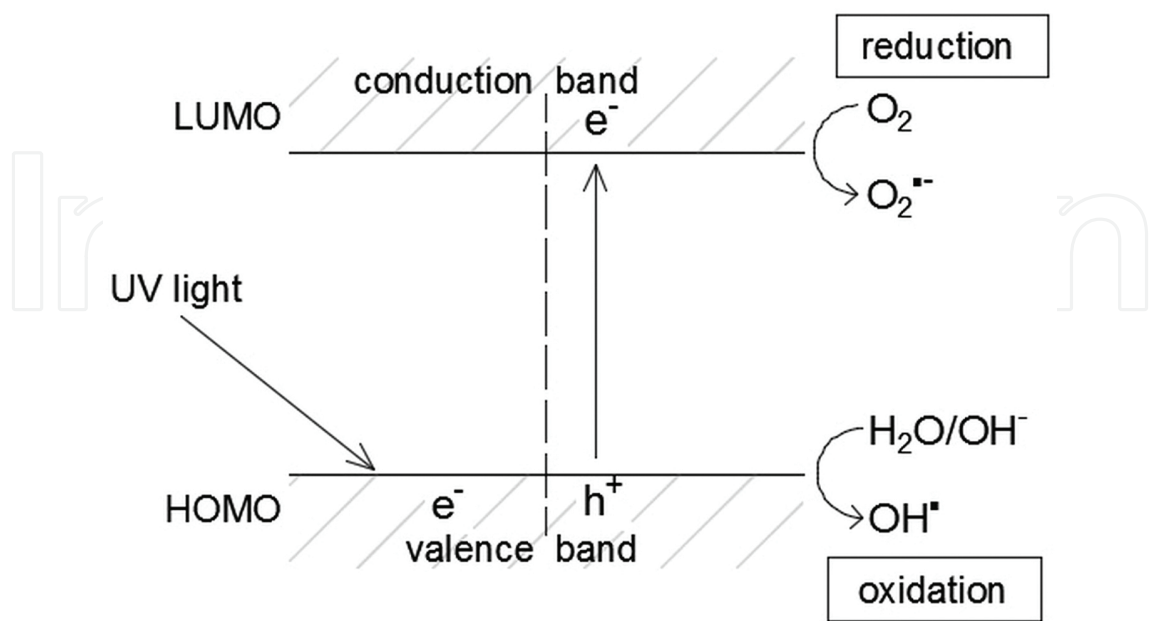
## 1. Introduction

In this chapter the information about photoactive concretes are shown. For many years the researchers were interested in preparation of modified building materials with the special properties. It was found that using titanium dioxide as additive to such materials gives them self-cleaning, antibacterial and antifungal properties, moreover it was found that in some cases the mechanical properties are also improved. This chapter contain five parts. First, the photocatalysis process is described. The mechanism of hydroxyl radical production during titanium dioxide irradiation is presented. In the literature, mainly the used method could be divided into three groups: the first group is when the concrete is covered by thin layer of  $\text{TiO}_2$  materials, e.g., paints or  $\text{TiO}_2$  suspensions. The second group is the concretes with thick layer

of photoactive concrete on the top. The third group is the concretes with different weight percent of  $\text{TiO}_2$  in the mass (substituted cement), then the results of photoactive tests of such materials are presented, mainly focused on the air cleaning from nitrogen oxides. Afterwards, the mechanical properties of photoactive concretes are presented. In this chapter,  $\text{TiO}_2$  effect on hydration process of cement,  $\text{TiO}_2$  effect on the compressive strength,  $\text{TiO}_2$  effect on carbonation of concretes, the fire resistance of photocatalytic concrete and the influence of  $\text{TiO}_2$  on abrasion resistance and shrinkage are presented. In the end of the chapter, the examples of building and objects built with using photoactive concretes are presented.

## 2. Description of photocatalysis process

The beginning of photocatalysis is considered a year of Fujishima and Honda article publication in 1972 [1]. The article presents the results of electrochemical photolysis of water at a semiconductor electrode. Although various definitions and interpretations of the term “photocatalysis” have been proposed, “photocatalysis” or “photocatalytic reaction” is defined by Ohtani [2] as a chemical reaction induced by photoabsorption of a solid material, or “photocatalyst”, which remains chemically unchanged during and after the reaction. The principle of photocatalysis is often explained with an illustration like **Figure 1**. An electron ( $e^-$ ) from the valence band (VB) is excited by photoirradiation to a vacant conduction band (CB). After excitation, a positive hole ( $h^+$ ) appears in the VB, these electrons and positive holes take part in the reduction and oxidation reactions of compounds adsorbed on the surface of a photocatalyst. The common photocatalyst is  $\text{TiO}_2$ . Then the possible ways for concretes modification are presented.



**Figure 1.** A schematic representation of the electronic structure of semiconducting materials.

The mechanism of the photocatalysis is summarized in Eqs. (1)–(12). First the production of electrons ( $e^-$ ) and holes ( $h^+$ ) in conduction band and valence band occurs (Eq. (1)). The photogenerated holes that escape direct recombination (Eqs. (3) and (4)) reach the surface of  $\text{TiO}_2$  and react with surface adsorbed hydroxyl groups or water to form trapped holes (Eq. (2)). The trapped hole ( $\equiv\text{TiO}^\bullet$ ) is usually described as a surface-bound or adsorbed  $\text{OH}^\bullet$  radical  $\text{OH}_{ads}^\bullet$ . According to (Eq. (7)),  $\text{OH}^\bullet$  generates at the surface of semiconductor and leaves the surface to bulk solution to form free  $\text{OH}^\bullet$  ( $\text{OH}_{free}^\bullet$ ). If electron donors ( $\text{Red}_{org}$ ) are present at the  $\text{TiO}_2$  surface, electron transfer may occur according to Eqs. ((5), (6) and (8)). In aerated systems, oxidative species, such as  $\text{O}_2^{\bullet-}$  and  $\text{H}_2\text{O}_2$  generate from the reduction site [3]:

charge-carrier generation:



hole trapping:



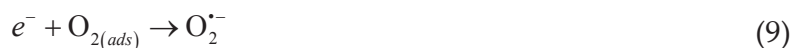
charge-carrier recombination:



charge transfer at the oxidation site:



charge transfer at the reduction site:



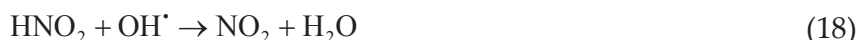
It is necessary to say that the photocatalysis process depends on: type and concentration of photocatalysts, type of eliminated contaminations, energy and intensity of used light. To determine the best possible conditions to perform photocatalytic process, all of these aspects are essential to consider. In the case of modified concrete, to have photocatalytic activity, most of tests are focused on air purification especially nitrogen oxide reduction and self-cleaning properties are tested during dyes decomposition.

For laboratory test of modified concrete activity, the nitrogen oxides are used. Below equations showed the mechanism of photocatalytic NO<sub>x</sub> oxidation on active concrete under UV illumination [4]. First the charge-carrier generation occurred (Eq. (1)).

The adsorption of the reactants onto the photocatalyst surface takes place:



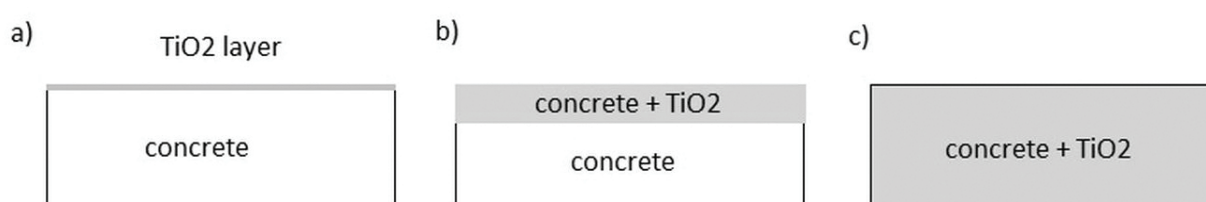
OH<sup>•</sup> radicals produced according Eqs. (7) and (12) take part in the nitrogen oxide oxidation, as follows:





### 3. The methods of modified concrete preparation

The methods of concrete preparation can be divided into three main groups (**Figure 2**). The first group is when the concrete is covered by thin layer of  $\text{TiO}_2$  materials, e.g., paints or  $\text{TiO}_2$  suspensions (**Figure 2a**). The second group is the concretes with thick layer of photoactive concrete on the top (**Figure 2b**). The third group is the concretes with different weight percent of  $\text{TiO}_2$  in the mass (substituted cement) (**Figure 2c**).



**Figure 2.** Scheme of possible ways for concrete modification by photocatalysts.

#### 3.1. The first group: the concrete is covered by thin layer of $\text{TiO}_2$

Chen and Chu [4] covered the surface of the concrete by a different types of the slurries. The authors tested eight application methods, five of them showed over 95% static NO reduction and over 89% static automobile exhaust (toluene, trimethylbenzene and nitrogen oxide) reduction. The slurries were brushed onto the surface of a previous concrete.

CWB—commercial water-based  $\text{TiO}_2$ .

CWLS—thin slurry with low cement concentration and  $\text{TiO}_2$  uniformly mixed together.

DIPM—a transparent liquid driveway protector (siliconate, water-based concrete sealer) and  $\text{TiO}_2$ .

TIW—water and  $\text{TiO}_2$  uniformly mixed.

PUR—PURETI commercial water based  $\text{TiO}_2$  applied to the surface with a special electrostatic sprayer.

Not only water is used for the slurry preparation, organic solvents are also used. Smits et al. [5] used ethanol to prepare dispersions. Photocatalyst was dispersed in ethanol (50 mg/ml) by sonication. The one layer of coating was performed by applying ethanol slurry on top of the mortar sample with the pipette. The coatings contain an equal amount of  $\text{TiO}_2$  ( $24 \pm 2$  mg) on samples' surface, equivalent to  $267 \mu\text{g}/\text{cm}^2$ . Building materials coated with  $\text{TiO}_2$  show self-cleaning properties as all coated samples are able to remove soot.

### 3.2. The second group: the concretes with thick layer of photoactive concrete on the top

These concretes consist two parts, lower layer is unmodified concrete, the top part of concrete consist cement with  $\text{TiO}_2$ . The amount of  $\text{TiO}_2$  used in the top layer is different for example Folli et al. [6] used about  $40 \text{ kg/m}^3$  of concrete. Under ideal weather and irradiation conditions, i.e. summer months, the monthly average NO concentration in proximity of the photocatalytic area was around 22% lower than the references are [6]. Fiore et al. [7] tested the concrete covered with photocatalytic cement mortar, with thickness of 3 and 5 mm. The results of the experimental tests have shown that the concrete carbonation depth can be significantly reduced by adopting photocatalytic surface layers. The results have also indicated that the application of titanium dioxide, modifies cementitious materials on the external surface of reinforced concrete elements, improves the corrosion performance of reinforcing bars in presence of carbonation of concrete.

### 3.3. The third group: the concretes with different weight percent of $\text{TiO}_2$ in the mass ( $\text{TiO}_2$ substituted cement)

In these examples, the titanium dioxide modified concrete in mass substitute cement. Usually the commercial titanium dioxide is used, for example: P25 (Evonic) or PC-105 (Millennium). The amounts of used photocatalysts: 0.5, 1, 2.5, 5 and 10 wt.% [8–10].

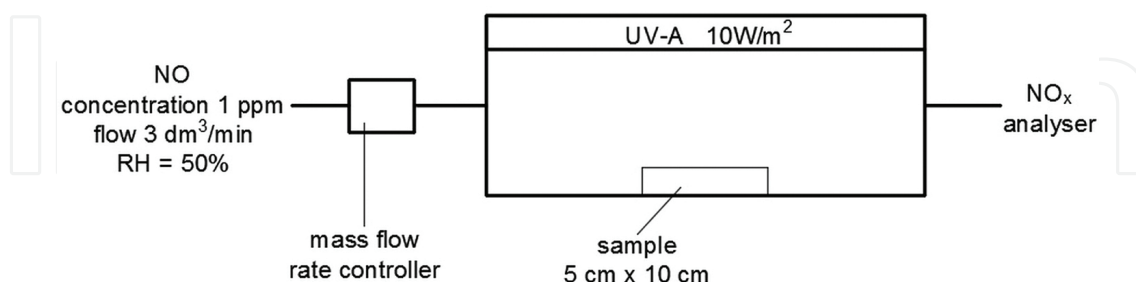
## 4. The results of photoactive tests

The activity of photoactive concretes is usually tested during an air purification especially  $\text{NO}_x$  removal. The self-cleaning properties are tested during dye removal from modified concretes surface. A lot of air purification tests are conducted according to method ISO 22197-1. The ISO standard employs an inert flat-bed photoreactor system designed to hold  $5 \times 10 \text{ cm}^2$  sample under illumination with UV-A light (irradiance =  $1 \text{ mW/cm}^2$ ). Humidified (RH = 50% at  $25^\circ\text{C}$ ) air and dry NO at concentration 1.0 ppm with flow  $3.0 \text{ dm}^3/\text{min}$  via mass flow rate controllers (Figure 3). The outlet gas stream from the reactor is sampled through a valve attached to a suitable  $\text{NO}_x$  detection system usually based on chemiluminescence [11].

Among the research concerning the transformation of the photocatalytic concrete materials to a larger scale the majority of the experiments refer to  $\text{NO}_x$  reduction, because the compounds are currently one of the main causes of a poor quality in large cities [7–9]. Blocks of the photocatalytic concrete are analysed towards the different features: the thickness of the photocatalytic layer, types of  $\text{TiO}_2$ , content of incorporated photocatalyst. It was also observed that in a real condition the blocks with more porous surfaces showed better results for the rate of  $\text{NO}_x$  degradation [12]. However, it is worth pointing out that apart from  $\text{NO}_x$  the volatile organic compounds (VOCs) are the target pollutants to remove using new concrete elements. Shen et al. [13] have made the attempts towards VOCs degradation during application of photocatalytic pavement.. Even though VOC displayed a significant variability in the removal efficiency, the reduction achieved level of nearly 90%. Other efforts were taken in a case of a durability of titanium dioxide photocatalyst coating for the concrete pavement. Hassan et al.



[14] determined abrasion and wear resistance properties of  $\text{TiO}_2$  coating and its effect on the coating environmental performance. The application of a special tester, which employs a scaled dynamic wheel passing back and forth over the sample, indicated on the acceptable durability and a wear resistance of the prepared photocatalytic concrete.



**Figure 3.** Photoreactor according to ISO 22197-1.



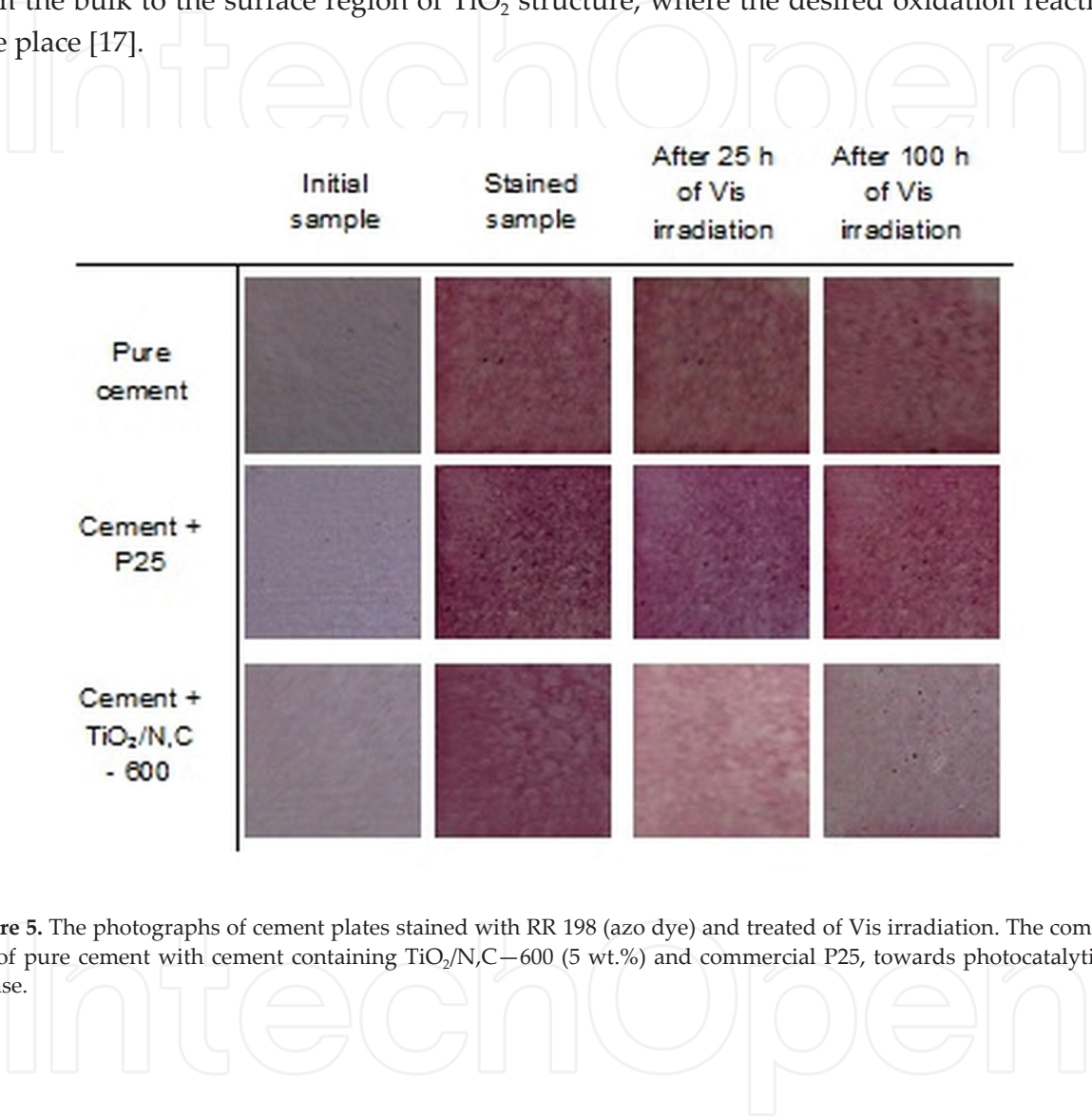
**Figure 4.** Separate parking lanes at the Leien of Antwerp with photocatalytic pavement blocks [15].

The scientific group Boonen et al. [15] performed the research in the laboratory and the pilot scale. As a result, the samples were active and the efficiency towards the reduction of  $\text{NO}_x$  increased with a longer contact time, a lower relative humidity and a higher intensity of light. Then they convert the results obtained in the laboratory scale to a real application. 10,000  $\text{m}^2$  of a photocatalytic pavement blocks were constructed on the parking lanes of a main road ace in Antwerp (**Figure 4**). The pavement demonstrated a good efficiency and durability towards  $\text{NO}_x$  abatement. Repeated measurements of the concrete pavement blocks confirm the efficiency after more than 5 years of using. It was observed the reduction in the efficiency due to the deposition of the nitrate on the surface. However, the original efficiency could be regained by washing the surface.

Most of the scientific works are focused on the commercial  $\text{TiO}_2$  as additives to the concretes. Some of the researchers tried to use a modified titanium dioxide as the additive. They found that carbon and nitrogen co-modified titanium added to the cement in the amount of 5%wt increased the photocatalytic activity of the concrete more than addition of the commercial P25.



The surface of a modified building material after covering by dyes and after 25 and 100 h of a visible light irradiation in **Figure 5** is presented. The higher activity of  $\text{TiO}_2\text{-N,C}$  is explained by the presence of the carbon and the nitrogen. It is generally claimed that the carbon doping improves the adsorption of the organic pollutants molecules on the catalyst surface. Moreover, the carbon doping can enhance the  $\text{TiO}_2$  conductivity, as it can facilitate the charge transfer from the bulk to the surface region of  $\text{TiO}_2$  structure, where the desired oxidation reactions take place [17].



**Figure 5.** The photographs of cement plates stained with RR 198 (azo dye) and treated of Vis irradiation. The comparison of pure cement with cement containing  $\text{TiO}_2\text{/N,C}$ –600 (5 wt.%) and commercial P25, towards photocatalytic response.

5. The results of mechanical properties of modified concretes

Photocatalytic concretes as a new functional materials are also studied in detail towards their mechanical properties. For a real wide application, the evaluation of a specific mechanical performance is required. It is worth stressed that the addition of  $\text{TiO}_2$  into concrete material can influence on some properties as a heat of hydration, a workability, a setting time, a chemical shrinkage, a mechanical strength, an abrasion resistance, a fire resistance, a freeze resistance, a water absorption, etc. [18].

### 5.1. TiO<sub>2</sub> effect on hydration process of cement

Our concerns about a nature of TiO<sub>2</sub> effect on the concrete should be started from the hydration process of the cement. It was proved that nano-TiO<sub>2</sub> acts not only as a photocatalyst but it is also a catalyst in the cement hydration reaction. Chen et al. [19] performed the detailed analyses of the hydration process in a case of the cement pastes and the mortars blended with TiO<sub>2</sub>. The TiO<sub>2</sub> particles acted as a potential nucleation sites for the accumulation of the hydration products. The addition of nano-TiO<sub>2</sub> powders significantly accelerated the hydration rate and promoted the hydration degree of the cementitious materials at the early ages. Simultaneously, TiO<sub>2</sub> was inert and stable during the cement hydration process. Meanwhile, the observed [20] acceleration of the hydration rate and changes of microstructure (after loading of TiO<sub>2</sub> into cement the total porosity of the cement pastes decreased and the pore size distribution was altered) affected the physical and the mechanical properties of the cement-based materials.

### 5.2. TiO<sub>2</sub> effect on the compressive strength

After loading of TiO<sub>2</sub> into cement, it was observed that the compressive strength of the mortar was enhanced (at early ages). The initial and final setting time was shortened and more water was required to maintain a standard consistence due to the addition of the smaller nano-TiO<sub>2</sub> particles. The relationship between hydration process and photocatalytic cementitious material properties was also by other scientists investigated [20–22]. However, other authors [23] the changes in mechanical properties in modified cementitious materials assigned to other phenomena. Using XRD technique they analysed the orientation index of CH crystal in different cement mortars with nano-TiO<sub>2</sub>. Test results indicated that when cement was substituted by nano-TiO<sub>2</sub> the strength of cement mortar at early ages increased a lot and the fluidity and strength at evening ages decreased. They claimed that the main reason for the improvement of strength is the decrease and modification of orientation index for the nucleation function, not the increasing amount of hydration products. Experimental data showed the entirely different tendency between the intensity of (0 0 1) crystal plane and that of (1 0 1) crystal plane for various samples without or with various photocatalysts. Namely, it was showed that the orientation index has an obviously effect on the strength of cement mortar.

The effect of loaded TiO<sub>2</sub> into cementitious materials might be considered from the point of view of microstructural changes as well. Lucas et al. [9] added a photocatalyst to mortars prepared with aerial lime, cement and gypsum binders to determine the way the microstructural changes affect the properties of the modified materials. In case of cement based mortar the porosity distribution was different between the mortar without and with TiO<sub>2</sub>. In the initial material the porosity distribution was divided in two intervals: a set of pores of larger size which ranged between 10 and 60 µm and another group between 0.02 and 1 µm. Up to 1 wt. % titania added to the cement matrix the compressive strength increased. Simultaneously, for these samples the larger pores completely disappeared remaining solely pores between 0.02 and 1 µm and the total porosity was reduced. The cement based mortar showed a mechanical strength reduction with increasing in additive content but the reduction was relatively low. It was explained by emerging a set of nanopores combined with the disappearance of the macropores. It clarified why the mechanical strength did not decrease so significantly. For the

maximum  $\text{TiO}_2$  content (5 wt.%), the nanoporosity increased notably and even with the presence of residual micropores (1.5–2.7  $\mu\text{m}$ ), the mechanical strength remained stable. In general, it was concluded that the presence of low size pores, particularly in the range between 1 and 0.1  $\mu\text{m}$  helps to minimize the detrimental effect of the loading of nanoadditives. Beside changes occurring during setting and hardening the microstructure of concrete and mortars evolves in time during the service life of structures [24]. Diamanti et al. [10] focused on mechanical and durability aspects of  $\text{TiO}_2$ -containing photocatalytic concrete by examining mutual influences between  $\text{TiO}_2$  and concrete components, and their evolution with the material aging. Materials were produced by adding the commercial form of  $\text{TiO}_2$  (P25) to concrete. In the beginning it was observed that despite the presence of nanoparticles which could play a positive filler effect, a slight decrease in a mechanical strength was observed in  $\text{TiO}_2$ -containing specimens. SEM analysis showed a slight increase in the concrete porosity and to a non-even distribution of  $\text{TiO}_2$  particles that in some cases were present as clusters.

According to Zhao et al. [25] the compressive strength was reduced with increase of titania content in cementitious composites. A 12% compressive strength reduction was observed when 10 wt.%  $\text{TiO}_2$  was added to the cement matrix. It was attributed to the flocculation of nano- $\text{TiO}_2$  particles which introduced a weak zone as flaws. In most papers is related that both, the strength and water permeability of the photocatalytic concrete are improved by adding  $\text{TiO}_2$  nanoparticles in the cement paste up to 2.0 wt.% [26], 3.0 wt.% [27] or 4.0 wt.% [28]. Ma et al. [29] studied the effects of nano- $\text{TiO}_2$  (NT) on the toughness of hardened mortars. The flexural and tensile strength of cement-based materials with different  $\text{TiO}_2$  dosage were tested. Results showed that the tensile and flexural strength increased with increasing NT content up to 3 wt.%. The appropriate amount of nanoparticles in mortars significantly improved the crystal orientation of CH between hardened cement pastes and aggregates and grain size of CH is also decreased, both of which can control the crystallization process of hydration products in an appropriate state. In addition, more compact C-S-H gels are formed under the nanometer hydration induction effect, which can significantly improve the mechanical properties of cement mortars. Using too high nanoparticles dosage, drying shrinkage distortions of mortars are enlarged, leading to more microcracks in the interface of hardened pastes and aggregates. Simultaneously, excess nano- $\text{TiO}_2$  is difficult to spread evenly and some internal defects would likely form in mortars.

During examination of new photocatalytic cementitious materials, the mechanical properties have been often estimated by compressive strength values. In order to present the tendency in effects, briefly, the table with results of several works was attached (**Table 1**). To obtain comparative results in each case the effect of analysis of reference material and material with the exemplary  $\text{TiO}_2$  dosage was shown. Mostly,  $\text{TiO}_2$  photocatalyst added in relatively low amount increased the compressive strength of cementitious materials. The mechanical properties measured in a form of the compressive strength were enhanced even 82 and 58% after 7 and 28 days of aging, respectively [27]. However, generally, the increase did not exceed the 10–12% determined at 7 days of curing or 18–23% in a case of 28 days.

Author	Exemplary TiO <sub>2</sub> dose (wt.%)	Age (days)	Compressive strength (MPa)	
			Reference sample	Photocatalytic sample
Nazari et al. [27]	4	7	20.6	37.6
		28	31.6	50.1
Nazari et al. [28]	3	7	16.0	27.4
		28	43.7	59.6
Noorvand et al. [46]	1.5	7	51.5	57.0
		28	64.0	76.2
Salemi et al. [26]	2	7	27.1	30.3
		28	42.1	51.7
Li et al. [47]	1	28	59.1	69.7
Behfarnia et al. [48]	1	28	35.7	28.3
Shekari et al. [35]	1.5	28	92.3	113.3

**Table 1.** Compressive strength of different photoactive cementitious materials.

### 5.3. TiO<sub>2</sub> effect on carbonation of concretes

The addition of TiO<sub>2</sub> led to a decrease in the resistance to carbonation in time. Increasing in carbonation coefficient was connected with the parallel, and analogous, decreasing in the compressive strength of tested materials. Carbonation has the primary negative consequence of inducing corrosion of an embedded steel reinforcement. It also leads to the changes in the microstructure of cement paste and in the composition in a pore solution [31]. It was showed [10] that on one side the presence of TiO<sub>2</sub> influenced the carbonation rate, while, on the other side, the carbonation induced modifications that have influenced the photoactivity of the materials. Self-cleaning efficiency decreased with the material aging, however, certain photoactivity was maintained, and the decreasing can be limited by increasing the initial amount of TiO<sub>2</sub>. The similar self-cleaning reduction was observed in a several works [20, 30] and was probably due to the shielding of TiO<sub>2</sub> nanoparticles by the carbonate precipitates and the obstruction of the surface pores. These work indicated that testing the properties of a freshly produced photocatalytic concrete materials is not indicative of their real behaviour. The experiments carried out after a few weeks, or the months, when the carbonation alters the surface, would give the proper information about the structures built with such materials. Some contradictory date, compared to the above described results, regarding the photocatalytic cement mortars, was obtained by Rao et al. [36]. The researchers used the self-compacting mortars with the addition of nano titanium in an amorphous state and 30% replacement of the cement with the fly ashes. First of all, the family mortars with nano-TiO<sub>2</sub> did not show any carbonation effect (or a relatively low carbonation depths) up to 91 days of the exposure in the accelerated carbonation chamber. Generally, in their results, the compressive strength increased with an age and decreased with the nanomaterials addition ratio.



#### 5.4. The fire resistance of photocatalytic concrete

The next clue issue is a fire resistance of the photocatalytic concrete. The normal concrete is a flameproof and reveals good resistance to the fire, though it is not considered as a refractory material. Biloxi et al. [32] examined the property of a white high performance concrete containing titanium dioxide. The concrete specimens were thermally treated at temperatures of 250, 500 and 750°C in an electrical radiant oven. The test results revealed number of significant variations in the mechanical strengths for the specimens exposed up to 250°C. However, the significant damage was observed for higher treatment temperatures, 500 and 750°C. The most important is that the similar observations were found for photocatalytic as well as for the ordinary concrete made with a similar aggregate. The effects of a damage were in the form of the microcracking. In the specimens treated up to 500°C, SEM images showed cracking of the concrete distributed randomly along the edges. In the specimens treated up to 750°C, the microcracks were more widespread and of larger dimensions. The only effect of high temperature on photocatalytic concrete, in a contrast to the original concrete, involved loss of photocatalytic capability at 750°C due to the transformation of titanium dioxide from anatase to rutile. Salemi et al. [26] focused on the frost resistance of the concrete containing various nanoparticles. In order to determine the property, the change in compressive strength, the change in the length, the loss of a mass and increasing in a water absorption in the specimens were measured during the cycle of a freezing and the thawing. The strength loss of the concrete containing nanoparticles appeared to be much lower than that of the plain concrete. The concrete containing 2 wt.% of nano-TiO<sub>2</sub> showed only 11.5% the strength loss after 300 cycles of freezing and thawing, while the strength loss of the plain concrete after 300 cycles was 100%. It is worth pointing out that the contribution of nano-TiO<sub>2</sub> in the improvement of the mechanical properties and durability of the concrete was higher than the other particles (e.g. Al<sub>2</sub>O<sub>3</sub>, ZnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>).

#### 5.5. Influence of TiO<sub>2</sub> on abrasion resistance and shrinkage

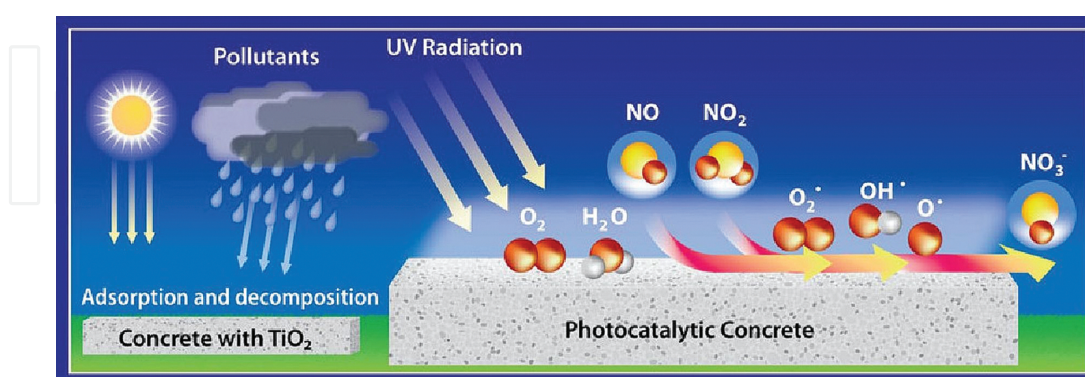
The influence of TiO<sub>2</sub> presence in a concrete on an abrasion resistance was studied by Li et al. [33]. The measurements were carried out after 28 days of curing in a standard moist room at the temperature 20°C. The test results indicated that the abrasion resistance of concretes containing nanoparticles was a significantly improved. The abrasion resistance of the concrete containing nano-TiO<sub>2</sub> in the amount of 1% by weight of a binder increased by 180% for the surface index. However, the effectiveness of TiO<sub>2</sub> in the enhancing abrasion resistance increased with the decrease of photocatalyst content (5 wt.% > 3 wt.% > 1 wt.%). The important observation is that the abrasion resistance of the concrete containing nanoparticles increased with the increasing the compressive strength and the relationship appeared to be a linear.

Regarding to the further mechanical properties of the concrete modified with titanium dioxide, it should be mentioned the influence of TiO<sub>2</sub> presence on a shrinkage, a workability and the setting time of the cementitious materials. Below was presented a general tendency of the impact. The inclusion of TiO<sub>2</sub> in the cementitious matrix increases the chemical shrinkage. The higher TiO<sub>2</sub> content resulted in a greater chemical shrinkage. It resulted from the directly relation and a proportionality to the degree of a hydration. The workability decreases with

increasing  $\text{TiO}_2$  content. It is probably related to the higher surface area of  $\text{TiO}_2$  particles that needs more water to wetting the cement particles. Similarly, as the content of photocatalyst increases as the initial and the final setting time decreases. This is explained by a rapid consumption of a free water speeded up to the bridging process of gaps and as a result, the viscosity increases and the solidification occurs earlier. There is also the possibility that due to the large surface area of photocatalyst a greater availability of nucleation sites is provided and leads to faster hydration rate and shorter setting time [18].

## 6. The examples of building and objects built with using photoactive concretes

In many studies, it was demonstrated that incorporation of titanium dioxide into the concrete materials is very effective solution towards degradation of a various hazardous and the toxic compounds. Therefore, its subsequent application in a real elements appeared to be a promising technology for the reduction in the environmental pollution. Among photocatalytic concrete products, it is worth to mention the pavement blocks, the tiles, and the walls of the buildings. The essential benefits of photocatalytic concrete elements are that it decomposes chemicals that contribute to soiling and air pollution, keep the concrete cleaner, and a reflect much of the sun's heat, because their white colour [34]. The construction materials might be the easily available medium to distribute photocatalysts over the widest surface area possible. It involves the high efficiency of the materials and simultaneously the increase in the materials costs is limited. Considering the self-cleaning attitude of the concrete materials it should be mentioned the simultaneous occurrence of two effects: photocatalytic degradation of deposits accumulating on their surface and photo-induced superhydrophilicity. As a consequence, the washing away of a reaction product is relatively easy [16]. The scheme of photocatalytic concrete action (example of  $\text{NO}_x$  degradation) was illustrated in **Figure 6** [15].



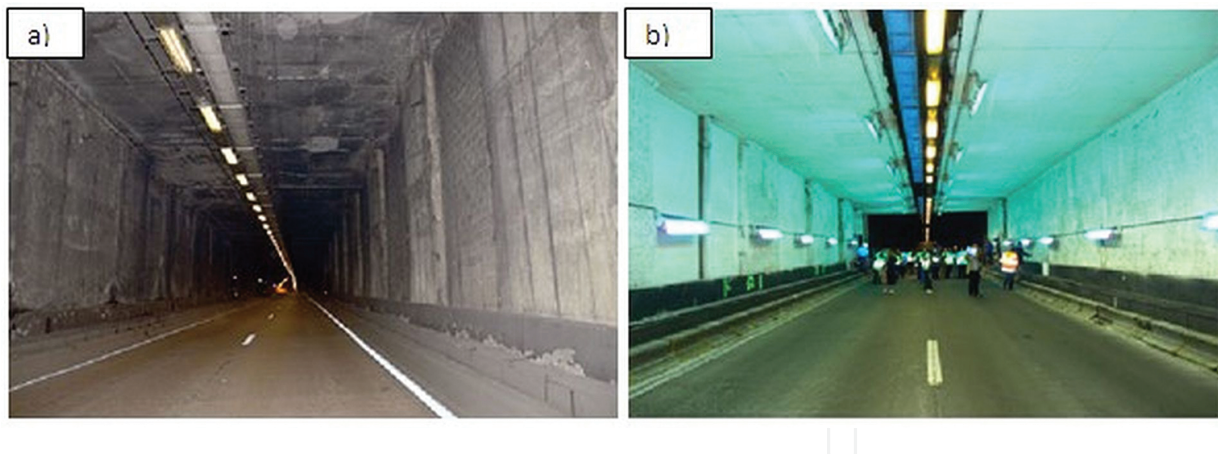
**Figure 6.** Scheme of photocatalytic air purifying pavement [15].

The first country where  $\text{TiO}_2$ -based cement has been marketed was Japan since the late 1990s [35, 37]. Nowadays, the white cement containing  $\text{TiO}_2$  is also used for the construction of buildings in Europe [16]. The patent of the application of  $\text{TiO}_2$  in pavement blocks is held by



Murata et al. (Mitsubishi Materials Corporation), as well as Cassar and Pepe (Italcementi S.p.A.) [38, 39]. Before we present the specific examples of buildings built from photocatalytic concrete, which exist in the world, we try to perform the studies focusing on the transformation from laboratory to real scale in a reference to the described materials.

The implementation of products, obtained in the laboratory, into a real scale demand taking into account a lot of parameters. On the final reduction rate of the pollutants influence the geometrical situation, the speed of the traffic, the speed and the direction of the wind, the temperature, humidity, etc. Namely, it is important that the exhaust gaseous pollutants stay in the contact with the photoactive surface during a certain period. Moreover, the real conditions require additional aspects of the new products connected with their multiple usages. In the case of a concrete pavement blocks, e.g.,  $\text{TiO}_2$  is placed in the whole thickness of wearing layer of the pavers. It means that even some abrasion takes place by the traffic, new  $\text{TiO}_2$  will be present at the surface to maintain the photocatalytic activity. Another possibility is using a double layered concrete with addition of  $\text{TiO}_2$ : in the mass and/or as dispersion on the surface [15]. The implementation efforts of the scientific group realizations [32] were taken in Belgium. Photocatalytic cementitious materials have been applied on the side walls and the roof of the Leopold II tunnel in Brussels. The states of the object before and after photocatalytic renovation were presented in **Figure 6**. About 100 m in length of the photocatalytic materials was applied. Inside the tunnel was observed the effect on the air pollution ( $\text{NO}_x$ , VOC's,  $\text{CO}_2$ ,  $\text{O}_3$ , etc.). A dedicated UV lightning system was installed inside the tunnel. which could be modulated (on/off) to directly see the action of the photocatalytic walls (see **Figure 7**).

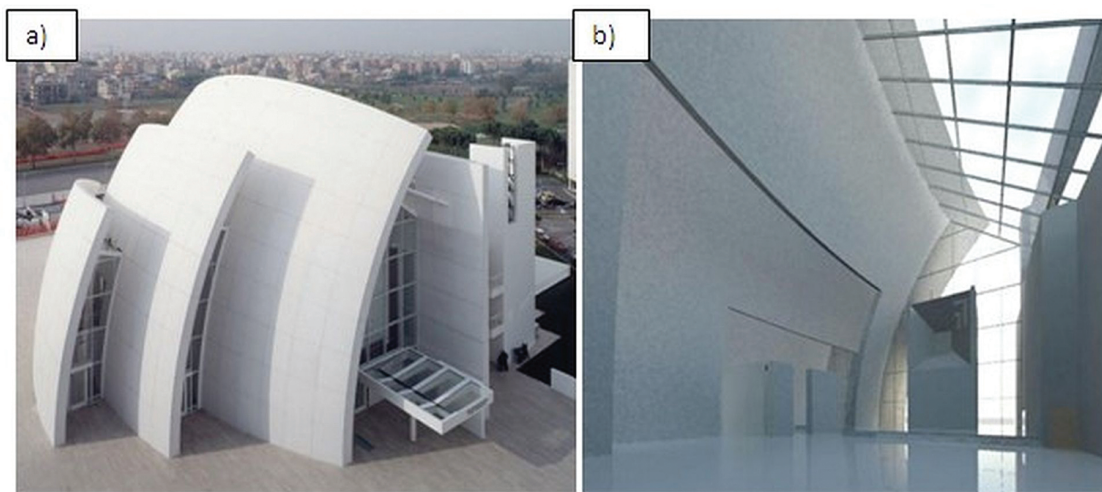


**Figure 7.** Inside view of test site within Leopold II tunnel in Brussels (a) before renovation, (b) after renovation with using photocatalytic walls [15].

Folli et al. [6] reported the results of a field test study concerning the use of photocatalytic paving elements in Denmark to decrease  $\text{NO}_x$  pollution. The large scale studies were preceded by the experiments in the lab. The test area was in a Copenhagen central street located close to the Central Railway Station. The test area involved 200 m long  $\times$  2 (both side of the road) sidewalk pavers. Hundred meter were built from ordinary concrete blocks and 100 m from concrete blocks containing titanium dioxide as a photocatalyst. Over the entire year, the daily

average NO concentration was maintained to very low values (below 40 ppb) in the area paved with the concrete elements containing  $\text{TiO}_2$ . The important aspect is that seasonal variation was observed. NO conversion decreased with increasing relative humidity as a result of competition between water and NO for catalytic sites. Meanwhile, NO conversion increased with increasing temperature due to a higher diffusivity of the gaseous pollutants towards the photocatalytic surface.

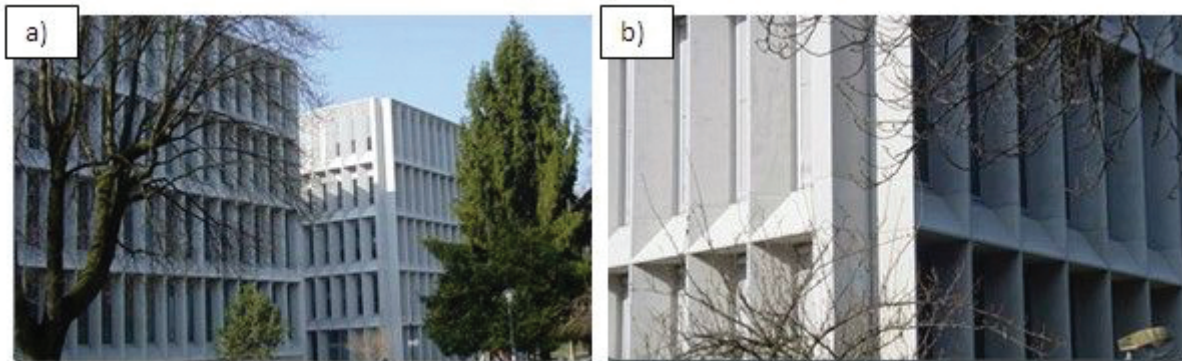
The experiments concerning a full-scale demonstration of air purifying pavement were also by Ballari and Brouwers [40] presented. In Hengelo, The Netherlands, the full width of the street was provided with concrete pavement containing  $\text{TiO}_2$  over a length of 150 m. The NOx concentration in the modified street and in control street together with weather parameters was measured. The results were directly connected with the weather conditions. Generally, the NOx concentration was 19% lower in comparison to the reference system. However, considering only afternoons or under high radiation and low relative humidity the value was 28% or 45% lower than in case of reference, respectively. The proposed solutions are promising techniques to reduce a number of air contaminants, especially at sites with a high level of pollution, such as: highly trafficked canyon streets or road tunnels.



**Figure 8.** Dives in Misericordia Church in Rome (a), zoom insight (b) [41].

Self-cleaning elements are mostly used in white concrete buildings. The first real project of building with the self-cleaning activity through  $\text{TiO}_2$  in cementitious materials was started in 1996 during realization of church Dives in Misericordia in Rome, Italy. The project was completed in 2003 by Italcementi S.p.A. — an Italian cement company (architect Richard Meier). The photos of the project were shown in **Figure 8**. It was found that over a six-year monitoring period, only a slight difference was observed between the white exterior and interior walls. The next clue example of objects built from photocatalytic cementitious material is Cité de la Musique et des Beaux-Arts in Chambéry, presented in **Figure 9**, which was completed in 2000. Monitoring for approximately five years indicated that in the Chambéry City Hall the primary colour remained almost constant in different facade position (on West, North, East and South)

[42, 43]. It is impressive that according to Fujishima and Zhang [44] by 2003, self-cleaning  $\text{TiO}_2$ -based tiles had been used in over 5000 buildings in Japan. Among them the most famous is the Maru Building, located in Tokyo's main business district.



**Figure 9.** Cité de la Musique et des Beaux- Arts in Chambéry [45].

## 7. Conclusions

The presented studies show that prepared concretes have photocatalytic activity and may purified an air from for example nitrogen oxides or the volatile organic compounds. Application of titanium dioxide into cement increased the mechanical properties of obtained concretes. Despite these advantage, some disadvantages unfortunately still exist.

1. Sometimes the by-products produce during photocatalytic decomposition of contamination are more toxic than substrates, it is possible to eliminate this by strong adsorption of by-products on the surface of photocatalysts until its overall mineralization.
2. The commercial photoactive cements are mainly activated under UV light irradiation; the researchers tried to find the photocatalyst active under visible light irradiation.
3. Increasing the weight addition of photocatalyst into cement, increasing its photocatalytic activity but mainly when the addition is higher than 5 wt.% the mechanical properties of modified cement decreased.
4. A price of the commercial photoactive cements (such as TioCEM®, Górażdże, Poland, TX Active®, Italcement Group, Italy) are still from eight to ten times more expensive than pure cement.

Beside these disadvantages, the advantages of new concretes as: air purification, better mechanical properties and self-cleaning properties, makes photoactive concretes the future building materials.



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