Air Purification Performance of Photocatalytic Concrete Paving Blocks after Seven Years of Service

Hubert Witkowski 1,*, Wioletta Jackiewicz-Rek 2, Karol Chilmon 2, Janusz Jarosławski 3, Anna Tryfon-Bojarska 4,5 and Arkadiusz Gasinski 6

1 Department of Building Physics and Building Materials, Lodz University of Technology, 90-924 Lodz, Poland
2 Faculty of Civil Engineering, Warsaw University of Technology, 00-637 Warsaw, Poland; w.jackiewicz-rek@il.pw.edu.pl (W.J.-R.); k.chilmon@il.pw.edu.pl (K.C.)
3 Institute of Geophysics, Polish Academy of Science, 01-452 Warsaw, Poland; januszj@igf.edu.pl
4 Skanska CDE, CEE Market, 00-877 Warsaw, Poland; anna.tryfon@skanska.pl
5 SGH Warsaw School of Economics, 02-554 Warsaw, Poland
6 Institute of Ceramics and Building Materials, 02-676 Warsaw, Poland; akgasin@gmail.com

* Correspondence: eng.hubert.witkowski@gmail.com; Tel.: +48-502-746-797

Received: 28 March 2019; Accepted: 15 April 2019; Published: 26 April 2019

Abstract: This paper presents the results of laboratory tests on photocatalytic pavement blocks from a bicycle lane in Poland after seven years of service. Air purification performance was tested on dusty and clean samples using different light sources and setups, with non-laminar gas circulation. Secondary Electrons Secondary Ions (SESI) and InLens detectors combined with SEM–EDS and X-ray analyses were applied to confirm the presence of TiO\(_2\) in the studied blocks. The obtained results show that TiO\(_2\) was present in the form of agglomerates with a diameter of 0.25–5 \(\mu\)m and was bonded to the cement matrix components. The tested samples still maintained nitric oxide (NO) removal capability with a NO reduction rate of 4–45%, depending on light source and surface cleanliness.

Keywords: photocatalytic concrete pavement; NO reduction; SEM analysis

1. Introduction

The problem of deteriorating air quality in urban areas has become one of the major challenges of recent times. With the rapid growth of metropolises, the problem of airborne pollution increases [1]. Considerable attention is therefore given to solutions that may reduce the concentration of harmful compounds, such as nitrogen oxides (NO\(_x\)), in the air. Short-term exposure to nitrogen dioxide (NO\(_2\)) leads to irritation of the upper respiratory tract, and long-term exposure to NO\(_2\) leads to chronic diseases. Nitric oxide (NO) is significantly less harmful to human health, however, in contact with air it oxidizes to form NO\(_2\).

The use of photocatalytic concrete in urban areas can contribute to a reduction in the concentration of NO\(_x\) in the air. Concrete is the most common construction material in use, hence its adoption to reduce the concentration of NO\(_x\) is a very promising solution.

The implementation of photocatalytic cement-based materials has been the subject of a number of research projects and applications across Europe and North America [2–6]. The photocatalytic properties of these materials are provided by the use of TiO\(_2\) nanoparticles in cement, or in surface suspension. The mechanism of the photocatalytic reaction of TiO\(_2\) has been described by Fujishima and Honda [7]. When TiO\(_2\) (semiconductor) is illuminated with high-energy photons, whose energy is equal to or greater than semiconductor band–gap energy, electrons transfer from the valence band to the conduction band. This starts a series of oxidation–reduction reactions with substances adsorbed on the semiconductor surface, which leads to the creation of hydroxyl radicals (OH) (Figure 1).
The following process of NOx reduction can be illustrated with the following equations:

\[
\text{NO} + \text{OH} \xrightarrow{\text{hv}, \text{TiO}_2} \text{NO}_2 + \text{H}^+ \quad (1)
\]

\[
\text{NO}_2 + \text{OH} \xrightarrow{\text{hv}, \text{TiO}_2} \text{NO}_3^- + \text{H}^+ \quad (2)
\]

On a concrete surface, NO$_3^-$ is created, which reacts with the cementitious compounds of concrete. Products of this reaction (nitric soils) are removed by rainwater from the concrete surface. As a result of this reaction, the concentration of nitric oxides in the vicinity of the surface is reduced, and the effect of air purification is observed.

The photocatalytic properties of concrete with the addition of TiO$_2$ have been proved in a number of laboratory studies [9–14]. The results of a research described by Beeldens [15] indicated that the major factors affecting the reaction are UV light intensity, surface exposure to UV light, pollutant concentration, ambient temperature, and air flow rate. As the research showed, the best results were obtained at high UV intensity, with a temperature above 25°C, with low relative humidity and low air flow.

Another important aspect is the durability of the air purifying capacity over time, especially in the case of pavement materials exposed to abrasion and soil. A case study of a street in Bergamo [16] indicated that paving blocks may still show a satisfactory air purification performance after two years of service. The same study also indicated that the effectiveness of the blocks was strongly dependent on surface cleanliness. Research showed that the reduction of NOx was significantly higher on days when the paving blocks were cleaned.

Unfortunately, the number of studies on air purification performance over time is very limited, particularly in relation to the effectiveness of the blocks after long-term usage in a moderate climate, where pavement materials are exposed not only to abrasion and soil, but also to cyclic freezing and thawing through the presence of deicing salt.

This paper presents the results of laboratory tests on pavement blocks collected from a bicycle lane in Zielona Gora (Poland). The aim of the study was to verify the air purification performance of photocatalytic concrete paving blocks after long-term service (seven years) in a moderate climate.

2. Experimental Procedure

Laboratory tests were conducted on two 330 × 150 × 80 mm exposed aggregate pavement blocks (Figure 2) collected after seven years of service from a bicycle lane that runs along one of the main roads in the city. The pavement blocks were collected from the 2m$^2$ area of the bicycle lane. The top layer (5 mm thick) of each sample was made of concrete containing CEM II/A–S 42.5 R (EN 197-1) with nano-TiO$_2$. The pavement blocks were produced in accordance with the EN 1339:2005 standard. The characteristic bending strength declared by the producer was 5.0 MPa (each single bending test resulted in no less than 4.0 MPa according to EN 1339:2005), and the declared water absorbability was less than 6%.
The characteristic bending strength declared by the producer was 5.0 MPa. The applied gas was a mixture of synthetic air (20% oxygen, 80% nitrogen) and NO in concentration of 100 ppb. The evaluation of the measurement was analogous to the procedure described by Husken et al. [10]. The NO abatement was defined as the ratio of the average NO concentration after turning the UV light on to the NO concentration before turning the UV light on. The flow rate in the research was less than 6%.

2.1. Test for Air Purification Performance

Samples were tested to determine photocatalytic activity with a special test setup. First, the concrete blocks were then examined with a Scanning Electron Microscope (SEM) using Energy Dispersive X-ray Spectroscopy (EDS) and SEM elemental mapping. The main objective of the research was to verify the photocatalytic properties after seven years of service.

The developed setup provided gas circulation analogous to the conditions in the real project. To determine the efficiency of photocatalytic materials in air purification, a number of different test procedures have been developed. The most often applied methods are ISO 22197-1:2016 [17], UNI–11247:2010 [18], and JIS TR Z 0018 [19]. Test methods assume laminar flow of the gas, as the distance between the sample and the glass window is very narrow (about 5 mm). Although such a set-up provides ideal conditions for measuring the reduction of NOx concentration at a constant gas flow, in real conditions the reaction of NOx reduction does not have the laminar character of a gas flow. Therefore, a novel setup (Figure 3) was developed to measure the air purification performance of the collected sample.

The developed setup provided gas circulation analogous to the conditions in the real project. The applied gas was a mixture of synthetic air (20% oxygen, 80% nitrogen) and NO in concentration of 100 ppb. The evaluation of the measurement was analogous to the procedure described by Husken et al. [10]. The NO abatement was defined as the ratio of the average NO concentration after turning the UV light on to the NO concentration before turning the UV light on. The flow rate in the research was 120 L/hour. The concentration of NO was measured with an API Model 200A NOx Monitor with an accuracy of ±5%. To provide UV light, two types of light source were applied: 70 W and
300 W. The reduction efficiency depends on the intensity of UV light, with a wave length in the range of 300–400 nm. The spectra obtained from each light source were therefore measured, including a measure of light spectra after passing the glass (Figure 4).

![Figure 4. Spectra obtained by applying two UV light sources. (a) Original spectra of 70 W bulb, (b) original spectra of 300 W bulb, (c) spectra after passing the desiccator glass, 70 W bulb, and (d) spectra after passing the desiccator glass, 300 W bulb.](image)

The tested concrete samples had to be cut to fit to the desiccators and had a diameter of 180 × 150 mm (270 cm²). The test procedure assumed achieving a maximum constant gas concentration of approximately 95 ppb in the desiccator, then the UV light was turned on for at least 20 min, and the reduction of NO was measured until a constant gas concentration was achieved. The average temperature of the measurement was 25°C with an average relative humidity of 50%.

2.2. SEM Analysis

For the SEM analysis, the Sigma VP (Zeiss), equipped with two EDS XFlash 6/10 (Bruker) detectors, was applied. As a standard, a voltage-accelerating electron beam of 15 kV was used. In the study of chemical composition with the EDS method, a 120 µm aperture was used, while for the high-resolution imaging, a 30 µm aperture was applied. The studied samples were collected from the concrete block surface. In order to ensure the discharge of electric charges on the surface of the test sample, the samples were sprayed with carbon and secured with a special strip of electrical charge. SEM tests were carried out in high-vacuum conditions (pressure < 1 × 10⁻⁵ Pa).

3. Results

The samples were tested according to the procedure and setup described. Therefore, the results cannot be compared to the results of standard tests.

3.1. NO Reduction

At the beginning, the samples were tested with a 70 W light source without any treatment (the samples were dusty). Then, the samples were cleaned with pure water, dried, placed again into the
glass desiccator, and tested with two different light sources. The results are presented in Figures 5–7 and Table 1.

Figure 5. Concentration of nitrogen oxides (NO\(_x\)) over time (dusty samples, 70 W light source).

![Graph showing concentration of NO\(_x\) over time](image)

Figure 6. Concentration of NO\(_x\) over time (cleaned samples, 70 W light source).

![Graph showing concentration of NO\(_x\) over time](image)

Table 1. Air purification performance test results.

| Light Source | 70 W  | 70 W  | 300 W |
|--------------|-------|-------|-------|
| Surface Cleanliness | Dusty | Cleaned | Cleaned |
| \(\Delta\)NO * | -4 ppb ± 1.3 | -5 ppb ± 0.3 | -43 ppb ± 1.0 |
| \(\Delta\)NO\(_2\) * | +3 ppb ± 0.6 | +2 ppb ± 0.5 | +9 ppb ± 3.1 |
| \(\Delta\)NO\(_x\) * | -1 ppb | -4 ppb | -34 ppb |
| \(\Delta\)NO\(_x\) * (\(\Delta\)NO + \(\Delta\)NO\(_2\)) | | | |
| NO reduction * % | 4% | 5% | 45% |

* mean results (±standard deviation) calculated from the maximum observed values during experiments for samples A and B.
The obtained results indicate that after seven years of service the tested paving blocks were still able to reduce NO content in the air (Table 1). The effectiveness of this phenomenon strongly depended on UV light intensity. The percentage of NO abatement was significantly higher when a 300 W light source was used. The surface cleanliness had a minor influence on NO abatement when the 70 W light source was used.

During the experiments, an increase of NO$_2$ content was observed. This phenomenon occurred, because of the complex characteristics of the photocatalytic process. Before NO finally oxidizes to NO$_3^-$ or HNO$_4$, the formation of HNO$_3$ and NO$_2$ occurs. NO$_2$ is about 5 to 25 times more toxic than NO [20]. This indicates that in some cases, the air quality may be degraded rather than improved. Therefore, when studying the air purification performance of photocatalytic materials, both NO removal and NO$_2$ formation must be considered [21]. The maximum average increase of NO$_2$ content was 8 ppb compared with a 43 ppb average reduction in NO content. Only in the case of weak light and a dusty sample was the $|\Delta$NO$_2|$ equal to $|\Delta$NO|.

### 3.2. SEM Analysis

SEM analysis allows for a precise examination of a sample surface. However, in the case of concrete with TiO$_2$ nanoparticles, such analysis is difficult. In the study, a Secondary Electrons Secondary Ions Detector (SESI) and an InLens detector were applied. An InLens detector was used to map the surface of the sample, and the SESI detector was used for images with fine detail. Using these detectors, it was possible to make morphological studies of particles and agglomerates, although the chemistry of these particle had to be confirmed by EDS analysis. EDS mapping was therefore performed first to indicate areas with a higher and lower content of titanium. Morphological studies of both types of area were then carried out using secondary electrons techniques. This approach enabled an investigation of the content of titanium dioxide and the morphology of its particles. Results are presented in Figures 8–10. The obtained images confirmed the presence of TiO$_2$ particles in the studied sample. Titanium dioxide was present in the form of agglomerates with a diameter of 0.25–5 µm. Titanium dioxide agglomerates were bonded to the compounds of the cement matrix.
The results of the tests on samples with different levels of surface cleanliness did not differ significantly. This was due to a UV light source which was not efficient (70W). After cleaning the sample and applying a more intense UV light source (300W), with better UV spectra, pronounced lighting with a combination of dirt on the photocatalytic material surface and low nitrate selectivity may contribute to the degradation of air quality.

Photocatalytic cementitious materials are a promising solution for the problem of deteriorating air quality, but taking into account the long service life of this type of elements (often much longer than the seven years of the tested samples), the efficiency of air purification should also be tested considering the presence of TiO$_2$ nanoparticles in the studied sample. Titanium dioxide was present in the form of agglomerates with a steady distribution in the tested sample. A chemical characterization of the compounds of the cement matrix. The obtained images confirmed the presence of titanium dioxide.

Figure 8. SEM image of the sample surface (SESI detector at ETH = 2.00 kV). (a) General view, (b) magnification of the selected area. Red arrows indicate TiO$_2$ agglomerates on the observed surface.

Figure 9. SEM image of the sample surface (InLens detector at ETH=2.00 kV). (a) Morphology, (b) EDS maps of titanium in the presented region.

Figure 10. (a) SEM image with indicated region of the X-ray analysis, (b) X-ray analysis of the indicated region.
For further analysis, scanning electron microscopy coupled with energy-dispersive spectrometry (SEM–EDS) was used to conduct quantitative X-ray analyses of the sample. To determine the places of X-ray analysis, an accurate sample EDS mapping of titanium was performed. The results of this analysis are presented in Figure 10. The obtained images and results indicate a steady distribution of TiO$_2$ agglomerates.

4. Conclusions

Laboratory tests confirmed the air purification performance of pavement blocks after seven years of service in a moderate climate. In accordance with the findings of Boonen and Beeldens [3], the ability to reduce the concentration of NO$_x$ in the air strongly depended on the UV light source. The results of the tests on samples with different levels of surface cleanliness did not differ significantly. This was due to a UV light source which was not efficient (70 W). After cleaning the sample and applying a more intense UV light source (300 W), with better UV spectra, pronounced abatement of NO was observed.

During the tests, an increase of NO$_2$ content was observed. Only in the case of the 70 W light source and a dusty sample was $|\Delta$NO$_2|$ (3 ppb) similar to $|\Delta$NO| (4 ppb), which indicated that weak lighting with a combination of dirt on the photocatalytic material surface and low nitrate selectivity may contribute to the degradation of air quality.

Images and mapping of SEM analysis confirmed the presence of TiO$_2$ in the form of agglomerates with a steady distribution in the tested sample. A chemical characterization of the sample with X-ray analysis also confirmed the presence of titanium dioxide.

Photocatalytic cementitious materials are a promising solution for the problem of deteriorating air quality, but taking into account the long service life of this type of elements (often much longer than the seven years of the tested samples), the efficiency of air purification should also be tested after longer intervals so as to confirm the usability of the technology throughout the period of use. The efficiency of this solution should also be verified on larger scale projects and in-situ studies, especially in the case of countries with a low UV index during most of the year.

Author Contributions: Conceptualization, H.W. and A.T.-B.; methodology and investigation, H.W., J.J., W.J.-R., K.C., A.G.; Writing—original draft preparation, H.W., W.J.-R., K.C.; Writing—review and editing, J.J., A.G.

Funding: This research was funded by Skanska Poland and Góraźdże Cement, as a part of research and implementation project on photocatalytic concrete.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Muilwijk, C.; Schrijvers, P.J.C.; Werz, S.; Kenjeres, S. Simulations of photochemical smog formation in complex urban areas. Atmos. Environ. 2016, 147, 470–484. [CrossRef]
2. Guerrini, G.L.; Beldens, A.; Crispino, M.; D’Ambrosio, G.; Vismaro, S. Environmental benefits of innovative photocatalytic cementitious road material. In Proceedings of the 10th International Conference on Concrete Pavement, Quebec City, QC, Canada, 8–12 July 2012. [CrossRef]
3. Boonen, E.; Beeldens, A. Recent Photocatalytic Applications for Air Purification in Belgium. Coatings 2014, 4, 553–573. [CrossRef]
4. Guerrini, G.L. Photocatalytic performance in a city tunnel in Rome: NOx monitoring results. Constr. Build. Mater. 2012, 27, 165–175. [CrossRef]
5. Boonen, E.; Akylas, V.; Barmpas, F.; Boreave, A.; Bottalico, L.; Cazaunau, M.; Chen, H.; Daele, V.; De Marco, T.; Doussin, J.F.; et al. Construction of a photocatalytic de-polluting field site in the Leopold II tunnel in Brussels. J. Environ. Manag. 2015, 155, 136–144. [CrossRef] [PubMed]
6. George, C.; Beeldens, A.; Barmpas, F.; Doussin, J.F.; Manganelli, G.; Herrmann, H.; Kleffmann, J.; Mellouki, A. Impact of photocatalytic remediation of pollutants on urban air quality. Front. Environ. Sci. Eng. 2016, 10, 1–11. [CrossRef]
7. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 1972, 238, 37–38. [CrossRef] [PubMed]
8. Wang, C.; Liu, H.; Qu, Y. TiO$_2$—Based Photocatalytic Process for Purification of Polluted Water: Bridging Fundamentals to Applications. *J. Nanomater.* 2013, 2013, 1–14. [CrossRef]
9. Shen, W.; Zang, C.; Li, Q.; Zhang, W.; Cao, L.; Ye, P. Preparation of titanium dioxide nano particle modified photocatalytic self–cleaning concrete. *J. Clean. Prod.* 2015, 87, 762–765. [CrossRef]
10. Husken, G.; Hunger, M.; Bruwers, H.J.H. Experimental study of photocatalytic concrete products for air purification. *Build. Environ.* 2009, 44, 2463–2474. [CrossRef]
11. Macphee, D.E.; Folli, A. Photocatalytic concretes—The interface between photocatalysis and cement chemistry. *Cem. Concr. Res.* 2016, 85, 48–54. [CrossRef]
12. Poon, C.S.; Cheung, E. NO removal efficiency of photocatalytic paving blocks prepared with recycled materials. *Constr. Build. Mater.* 2007, 21, 1746–1753. [CrossRef]
13. Cassar, L.; Beeldens, A.; Pimpinelli, N.; Guerrini, G.L. Photocatalysis of cementitious materials. In Proceedings of the International RILEM Symposium on Photocatalysis, Environment and Construction Materials, Florence, Italy, 8–9 October 2012.
14. Chen, J.; Poon, C. Photocatalytic construction and building materials: From fundamentals to applications. *Build. Environ.* 2009, 44, 1899–1906. [CrossRef]
15. Beeldens, A. An environmental friendly solution for air purification and self-cleaning effect: The application of TiO$_2$ as photocatalyst in concrete. In Proceedings of the 8th International Conference on Concrete Blocks Paving, San Francisco, CA, USA, 6–8 November 2006.
16. Guerrini, G.L. Some observations regarding in–service performance Photocatalytic paving block surfaces. *Betonwerk Fertigteil-Technik BFT* 2009, 5, 16–25.
17. ISO 22197-1:2016, Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics)—Test Method for Air-Purification Performance of Semiconducting Photocatalytic Materials—Part 1: Removal of Nitric Oxide; ISO: Geneva, Switzerland, 2016.
18. UNI-11247:2010, Determination of the Degradation of Nitrogen Oxides in the Air by Inorganic Photocatalytic Materials: Continuous Flow Test Method; Ente Nazionale Italiano di Unificazione: Milano, Italy, 2010. (Italian Standard).
19. JIS TR Z 0018, Photocatalytic Materials—Air Purification Test Procedure; Japanese Standards Association: Tokyo, Japan, 2002. (Japanese Standard).
20. Folli, A.; Macphee, D.E. Future challenges for photocatalytic concrete technology. In Proceedings of the 34th Cement and Concrete Science Conference, University of Sheffield, Sheffield, UK, 14–17 September 2014.
21. Bloh, J.; Folli, A.; Macphee, D. Photocatalytic NO$_x$ abatement: Why the selectivity matters. *RSC Adv.* 2014, 4, 45726–45734. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).