

Photocatalytic roads: from lab tests to real scale applications

Elia Boonen · Anne Beeldens

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Abstract

Purpose This paper gives an overview of our research on photocatalytic concrete, which exhibits air purifying properties. Under the action of sunlight, a catalyst present at the surface of the material is activated, enabling degradation of pollutants from the surroundings and transformation to less harmful products. It is a promising technique to reduce a number of air contaminants, especially at sites with a high level of pollution: highly trafficked canyon streets, road tunnels, etc. In addition, the combination with cement offers some synergistic advantages, as the reaction products can be adsorbed at the surface and subsequently washed away by rain. However, the great potential of this emerging technology is hampered by the lack of uniform testing methods at European level to evaluate the photocatalytic activity.

Methods Laboratory research is undertaken at BRRC to compare existing methods and draw up recommendations for future standards. Furthermore, translation of lab testing towards results in situ remains critical to demonstrate the effectiveness on larger scale. In this perspective, several trial applications have recently been initiated in Belgium to assess the “real life” behavior.

Results The paper gives a short overview of the photocatalytic principle and the application in concrete, as well as some main results of the laboratory research recognizing the important parameters that come into play. In addition, the implementation efforts of some recent realizations in Belgium will be presented.

Conclusions Already some very promising results towards air purification have been obtained. Nevertheless, further validation, also with modeling, is necessary to extrapolate the findings and enable a judicial implementation of photocatalytic road materials across the globe.

Keywords Concrete roads · Air (de-) pollution · Heterogeneous photocatalysis · Titanium dioxide · Nitrogen oxides

1 Introduction

Emission from the transport sector has a particular impact on the overall air quality because of its rapid rate of growth: goods transport by road in Europe (EU-27) has increased by 31 % (period 1995–2009), while passenger transport by road in the EU-27 has gone up by 21 % and passenger transport in air by 51 % in the same period [1]. The main emissions caused by motor traffic are nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO), accounting for respectively 46 %, 50 % and 36 % of all such emissions in Europe ann. 2008 [2].

These pollutants have an increasing impact on the urban air quality. In addition, photochemical reactions resulting from the action of sunlight on NO₂ and VOC's (volatile organic compounds) lead to the formation of ‘photochemical smog’ and ozone, a secondary long-range pollutant, which impacts in rural areas often far from the original emission site. Acid rain is another long-range pollutant influenced by vehicle NO_x emissions and resulting from the transport of NO_x, oxidation in the air into NO₃⁻ and finally, precipitation of nitric acid with harmful consequences for building materials (corrosion of the surface) and vegetation.

The European Directives [3] impose a limit to the NO₂ concentration in ambient air of maximum 40 µg/m³ NO₂

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E. Boonen (✉) · A. Beeldens
Belgian Road Research Centre (BRRC),
Fokkersdreef 21,
1933 Sterrebeek, Belgium
e-mail: e.boonen@brcc.be

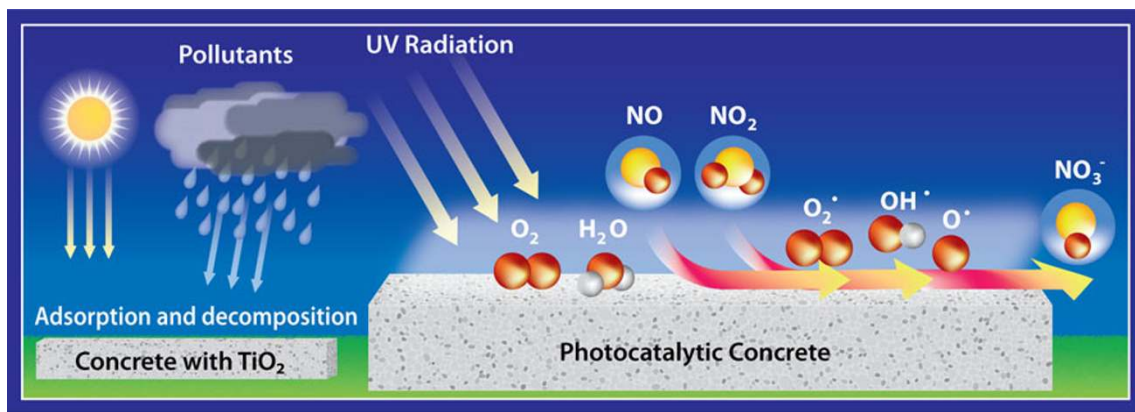


Fig. 1 Schematic of photocatalytic air purifying pavement

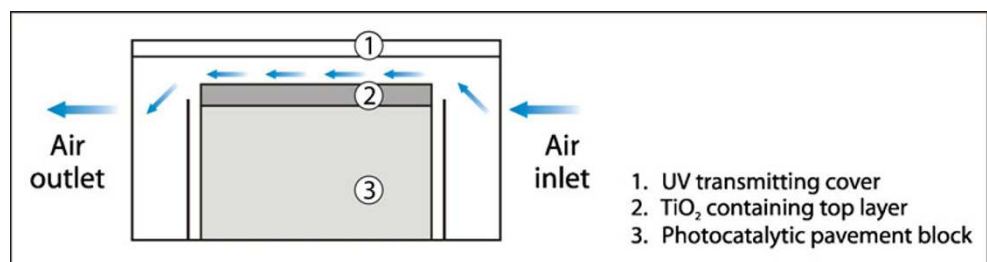
(33 ppbV) averaged over 1 year and $200 \mu\text{g}/\text{m}^3$ (163 ppbV) averaged over 1 h. These limit values gradually decreased from 50 and 250 in 2005 to the final limit in 2010.

Heterogeneous photocatalysis is a promising method for NO_x abatement. In a first part of this paper, the principle of photocatalytic materials will be elaborated, followed by a description of the past laboratory research indicating important influencing factors for the purifying process. Next, an overview of the results regarding the first pilot project in Antwerp [2] is given, and finally, different applications in Belgium that have recently been started, will be discussed.

2 Heterogeneous photocatalysis, a process for air purification

A solution for the air pollution by traffic can be found in the treatment of the pollutants as close to the source as possible. Therefore, photocatalytically active materials can be added to the surface of pavement and building materials [4]. In combination with (sun) light, the pollutants are oxidized and/or reduced due to the presence of the photocatalyst and precipitated on the surface of the material. Afterwards, they can be removed from the surface by the rain or cleaning/washing with water, see Fig. 1.

Fig. 2 Schematic and photo of measurement set-up according to ISO 22197-1:2007 [12] at BRRC



Heterogeneous photocatalysis with titanium dioxide (TiO_2) as catalyst is a rapidly developing field in environmental engineering, as it has a great potential to cope with the increasing pollution. The impulse for the use of TiO_2 as photocatalyst was given by Fujishima and Honda in 1972 [5]. They discovered the hydrolysis of water in oxygen and hydrogen in the presence of light, by means of a TiO_2 -anode in a photochemical cell. In the eighties, organic pollution in water was also decomposed by adding TiO_2 and under influence of UV-light (with wave lengths lower than 387 nm). The application of TiO_2 , in the photoactive crystal form anatase, as air purifying material originated in Japan in 1996 (see e.g. [6]). Since then, a broad spectrum of products appeared on the market for indoor use as well as for outdoor applications. Regarding traffic emissions, it is important that the exhaust gases stay in contact with the active surface during a certain period. The geometrical situation, the speed of the traffic, the speed and direction of the wind, the temperature, all influence the final reduction rate of pollutants in situ.

In the case of concrete pavement blocks [7, 8], the anatase is added to the wearing layer of the pavers which is approximately 8 mm thick. The fact that the TiO_2 is present over the whole thickness of this layer means that even if some abrasion takes place by the traffic, new TiO_2 will be present at the surface to maintain the photocatalytic activity. Another, similar application consists of using a double layered concrete with addition of TiO_2 (in the mass and/or as dispersion on the surface) to the top layer, which will be discussed later on. The use of TiO_2 in combination with cement leads to a transformation of the NO_x into NO_3^- , which is adsorbed at the surface due to the alkalinity of the concrete [9]. Thus, a synergetic effect is created in the presence of the cement matrix, which helps to effectively trap the reactant gases (NO and NO_2) together with the nitrate salt formed. Subsequently, the deposited nitrate will be washed away by rain.

Up till now, UV-light (in the UV-A spectrum) was necessary to activate the photocatalyst. However, recent research indicates a shift towards the visible light [10]. This means that applications in tunnels and indoor environments become more realistic. Especially the application in tunnels is worth looking at due to the high concentration of air pollutants at these sites. One of the projects in Belgium is focusing on this subject [11].

3 Laboratory results: parameter evaluation

Different test methods have been (and still are being) developed to determine the efficiency of photocatalytic materials towards air purification. An overview is given in [9]. A distinction can be made by the type of air flow; in the flow-through method according to ISO 22197-1 [12], the air, with a concentration of 1 ppmV of NO, passes over the

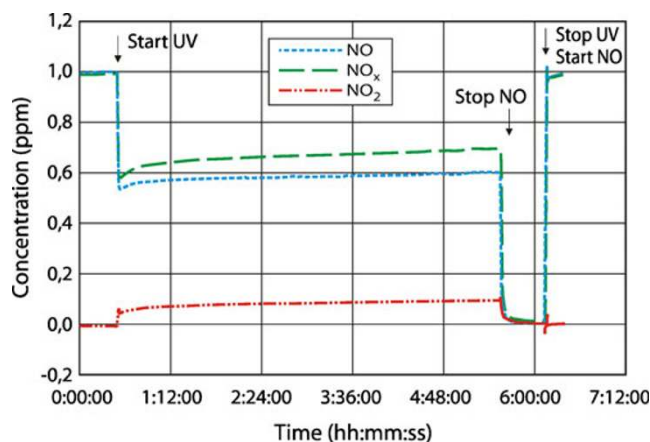


Fig. 3 Typical result obtained in laboratory according to the standard ISO test procedure

sample which is illuminated by a UV-lamp with light intensity equal to 10 W/m^2 in the range between 300 and 400 nm, as illustrated in Fig. 2. Afterwards, the NO_x concentration is measured at the outlet. It is also worth to note here that within Europe actions are underway to harmonize and develop new standards for photocatalysis [13]. Specifically concerning NO_x abatement, investigations are currently being made, also at the BRRC, into a new type of mixed reactor system which could offer some advantages in the future. In any case, the test procedure used for the current results is following the existing ISO-standard.

The preparation of the samples is of great importance. Due to the photocatalytic activity NO_3^- is deposited on the surface and covers to a certain extent the TiO_2 from the light and pollutants. Consequently, the efficiency is lowered over time, but by rinsing the surface, the initial efficiency can be restored again as also demonstrated later on. The pre-treatment of the samples in the laboratory can be important to obtain reproducible results and mainly depends on the type of base material. In the case of concrete, the release of NO and NO_2 prior to the photocatalytic reaction is limited; in the case of paints however, this can be more important. A

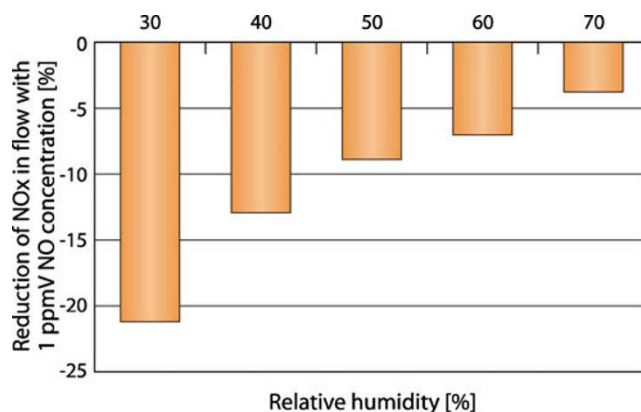


Fig. 4 Effect of relative humidity on photocatalytic efficiency

Fig. 5 Separate parking lanes at the Leien of Antwerp with photocatalytic pavement blocks



typical test scheme according to the ISO standard is represented in Fig. 3, where the following steps are applied to the sample: 0.5 h at 1 ppmV NO concentration, no light – 5 h exposure to an air flow of 3 l/min with 1 ppmV NO and UV-illumination – 0.5 h with UV-illumination and no exposure. A small increase in time of the NO_x concentration is visible due to the deposit of the NO₃⁻ at the surface.

In the laboratory, the influence of different important test parameters affecting the photocatalytic reaction has been investigated [2] such as temperature, light intensity, relative humidity, contact time (controlled by surface area, flow velocity, height of air flow ...). For instance, the effect of relative humidity of the ingoing air is illustrated in Fig. 4. Clearly, the reduction of the NO_x concentration in the outlet air decreases with increasing relative humidity (RH %). This has to do with the fact that the water in the atmosphere plays a role in the adhesion of the pollutants at the surface and with the competition effect that can arise between water molecules and NO_x in the ambient air with increasing RH. Hence, relative humidity is an important limiting factor for photocatalytic applications in humid areas like Belgium.

In general, it can be stated that the efficiency towards the reduction of NO_x increases with a longer contact time (larger surface area, lower air velocity, smaller height of air flow, higher turbulence at the surface), a lower relative humidity and a higher intensity of incident light. These are the conditions at which the risk of ozone formation in summer is the largest: high temperatures, no wind and no rain. At these days, the photocatalytic reaction will be more pronounced.

4 Pilot project in Antwerp

An important issue is the conversion of the results obtained in the laboratory to real applications. In order to see the influence of photocatalytic pavements in “real life”, a first pilot section of 10.000 m² of photocatalytic pavement blocks was constructed in 2004–2005 on the parking lanes of a main road axe in Antwerp. Figure 5 gives a view of the parking lane, where the photocatalytic concrete pavement blocks have been applied. Only the wearing layer of the blocks contains TiO₂. In spite of the fact that the surface

Fig. 6 NO_x concentration at the outflow, measured on 2 pavement blocks, *before* (hatched) and *after* (colored) washing the surface. Measurements correspond to different pavement blocks taken from the test site in Antwerp at different periods of time

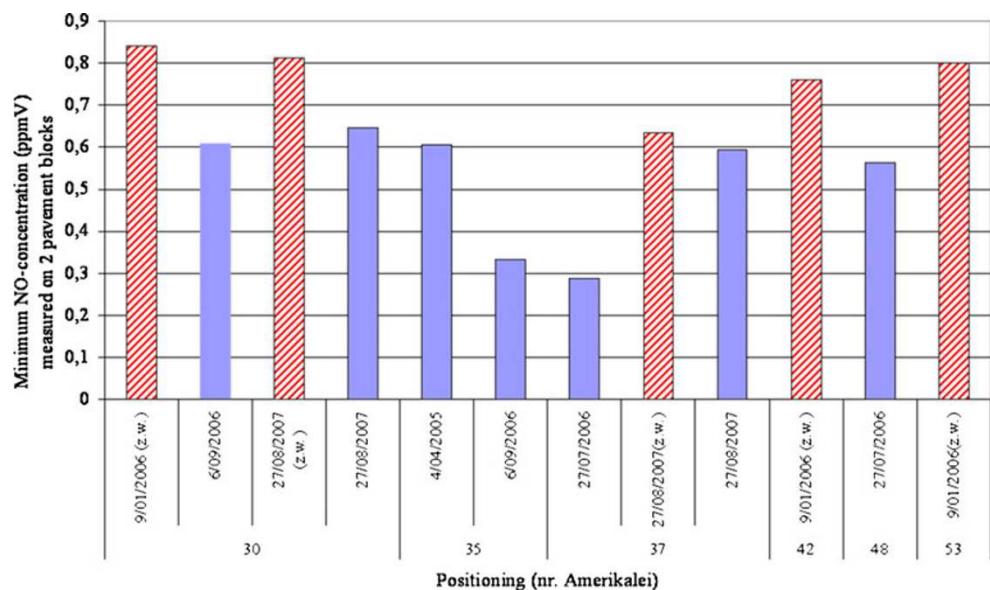
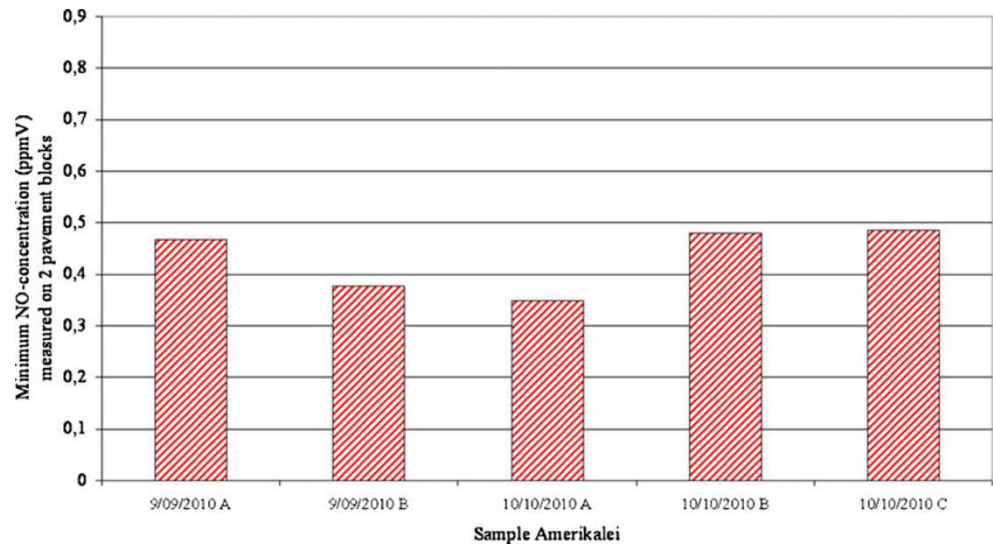


Fig. 7 Measurements on pavements blocks in 2010, all before washing, after 5 years of service life



applied on the Leien of Antwerp is quite important, one has to notice the relative small width of the photocatalytic parking lane in comparison with the total street: 2*4.5 m on a total width of 60 m.

Two different types of tests were carried out. First of all, pavement blocks were taken from the Leien after different periods of exposure. These blocks were measured in the laboratory with and without washing of the surface. The results are presented in Fig. 6 and, despite the variability in results which is probably due to the different previous history of the pavers (accumulation of dirt, rain fall, sun shine,...), they demonstrate a good durability of the efficiency towards NO_x abatement. The deposition of pollutants on the surface leads to a decrease in efficiency which can be regained after washing. To check the longevity of the photocatalytic action, measurements were recently (in 2010)

repeated on in situ removed paving stones, as shown in Fig. 7. The results indicate that even after more than 5 years of service life, the durability of the photocatalytic pavers still persists.

Besides the tests in the lab, on site measurements were also carried out. Since no reference measurements without photocatalytic material (prior to the application) exist, the interpretation of these results is rather difficult. Especially the influence of traffic, wind speed, light intensity and relative humidity are playing an important role. Detailed results can be found in [2]. In brief, the field measurements suggested a decrease in NO_x concentration at the sites with photocatalytic materials, where a levelling out of the peaks is visible. In any case, precaution has to be taken with the interpretation of data since these results are momentary and limited over time. But, at least, they give an indication of the

Fig. 8 NO-reduction under visible light as a function of different intensities [14]

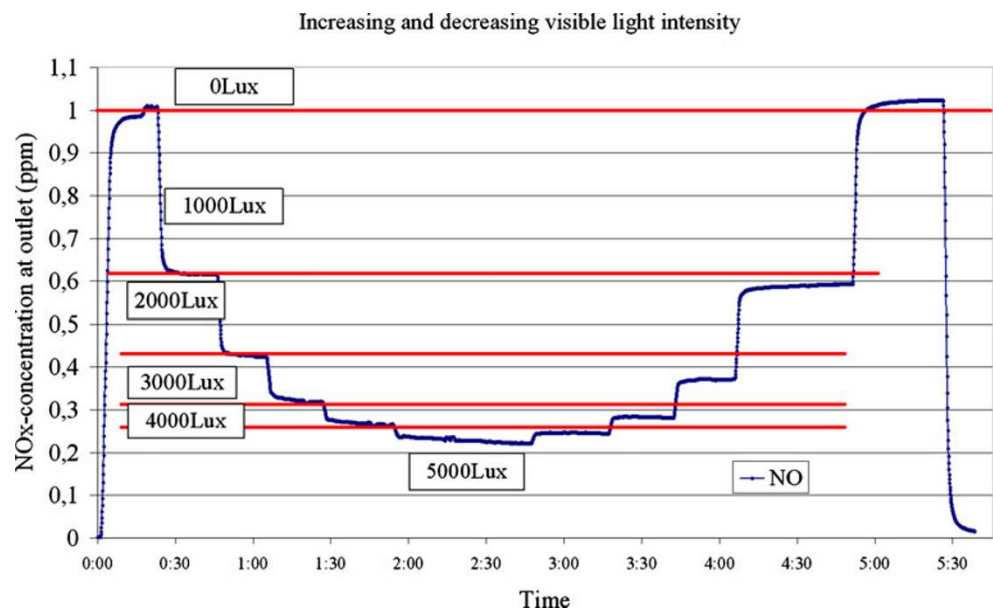




Fig. 9 Inside view of test site within Leopold II tunnel in Brussels, before renovation

efficiency of the photocatalytic pavement materials in situ, and a basis to work on for future applications.

5 Recent photocatalytic applications in Belgium

Since the first application in Antwerp (2004–2005), much progress has been made within the photocatalytic research area. Newer, better and more efficient materials are constantly being developed, and action is more and more broadened also to visible light responsive materials. An example of such a material is given in Fig. 8 [14]. Hence, the need still exists to develop more in situ applications in which the relation between the efficiency in laboratory and on site is established, e.g. [15, 16, 17]. An overview of two such recent projects in Belgium is given in this section.

5.1 Life⁺-Project PhotoPAQ

The European Life⁺-project PhotoPAQ, *Demonstration of Photocatalytic remediation Processes on Air Quality* [11], is aimed at demonstrating the usefulness of photocatalytic (road) construction materials for air purification purposes in an urban environment. Within this consortium, consisting of 8 partners coming from 5 different countries, two extensive field campaigns will be organized within Europe, of

Fig. 10 Leopold II tunnel test site, after renovation in September 2011 and dedicated testing equipment



which one in Belgium. For the latter, photocatalytic cementitious materials have been applied on the side walls and roof of the Leopold II tunnel in Brussels (see Fig. 9).

A test section of about 100 m in length was installed in August 2011, see Fig. 10. Afterwards, an intensive measurement campaign with specific testing equipment took place from 8th till 23th of September 2011 to rigorously assess the effect on the air pollution (including NO_x, VOC's, Particulate Matter, CO₂, O₃...). To this end, a dedicated UV-lighting system (see also Fig. 10) was installed inside the tunnel which could be modulated (on/off) to directly see the action of the photocatalytic walls. Concurrently, simulations of the tunnel air flow are performed in order to model the abatement of pollutants and the effect of different influencing parameters (traffic flow, concentration profiles, ventilation...). This modeling, when validated with the measurements, could provide a valuable tool for extrapolation of the findings to other sites.

5.2 INTERREG Project ECO2PROFIT

The broad environmental sustainability project ECO2PROFIT deals with the reduction of the emission of greenhouse gasses and sustainable production of energy on industrial estates in the frontier area between Flanders and Holland. To reach these goals, several tangible demonstration projects have been planned on industrial sites in Belgium and the Netherlands.

One particular project is situated on the industrial zone “Den Hoek 3” in Wijnegem (near Antwerp). Here, the regional development agency POM Antwerp is aiming to use a double layered concrete for the road construction, with recycled concrete aggregates in the bottom layer and photocatalytic materials (TiO₂) in the top layer. That way, air purifying and CO₂ reducing concrete roads can be built which are both innovating and energy efficient. For this project the BRRC was asked to set-up an elaborate testing program in the lab to help optimize the air purifying performance of the top layer, without interfering with other properties of the concrete (workability, mechanical, durability...).



Fig. 11 Trial section of double layered concrete with TiO_2 in the top layer on industrial zone “Den Hoek 3” in Wijnegem

Furthermore, a trial section was constructed, as shown in Fig. 11, to get familiar with the technique of constructing two-layered concrete.

For the application of photocatalytic materials in a concrete road (and in general for any other type of application) a fundamental choice can be made between: mixing in the mass (TiO_2 in cement) and/or spraying on the surface (dispersion of TiO_2). The former has the advantage of a more durable action since the TiO_2 will continuously be present, even after wearing of the top layer. On the other hand, the initial cost will be higher (higher TiO_2 content, necessity for double layered concrete) and only the TiO_2 at the surface will be active. In contrast, dispersing at the surface of a TiO_2 solution will provide a more direct action, and a lower initial cost (e.g. “ordinary” cement). In this case however, the longevity of the photocatalytic action could be questioned because of loss of adhesion to the surface in time. This fundamental choice was also investigated within the research programme.

For reasons of noise reduction and comfort of the road user, it was decided to use an exposed aggregates surface finish (grain size 0/6,3) for the top layer (see right side of

Fig. 11). In a first phase, an optimization of the concrete composition for both layers had to be performed in terms of workability (“ideal” grading curve), mechanical properties (compression strength), and durability (resistance against frost/thaw cycles), as illustrated in Fig. 12.

Subsequently, trial sections of 30 m long and 3 m wide (left side of Fig. 11) were constructed to assess the feasibility of using the double layered technique in practice. In this stage, a “normal” cement was used (no mixing of TiO_2 in the mass) while a photocatalytic dispersion was sprayed over the exposed aggregates surface, after application of a curing compound. In addition, some first tests towards the air purifying performance of the concrete surface were made. To this end, test plates were also made on site using the concrete of the top layer and with application of the photocatalytic dispersion. After construction, these plates were kept under atmospheric conditions for 20 days, and subsequently cut to size and stored at $\text{RH}=(60\pm 2)\%$ and $T=(20\pm 2)^\circ\text{C}$ for 15 days. Finally, the samples were tested for their photocatalytic efficiency with the set-up of Fig. 2 and

Fig. 12 Optimization of concrete composition for top layer to approach the “ideal” inert skeleton (dotted curve)

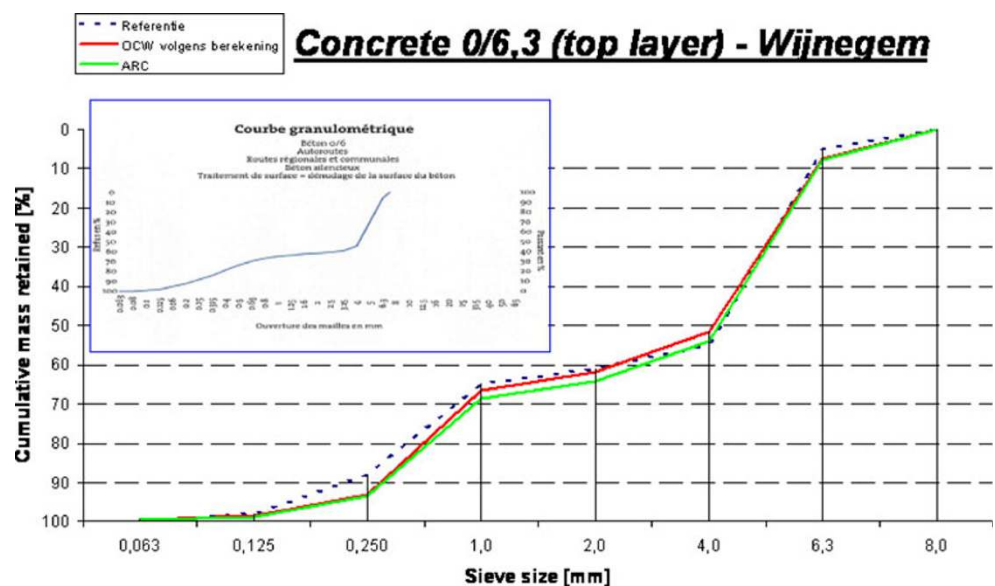
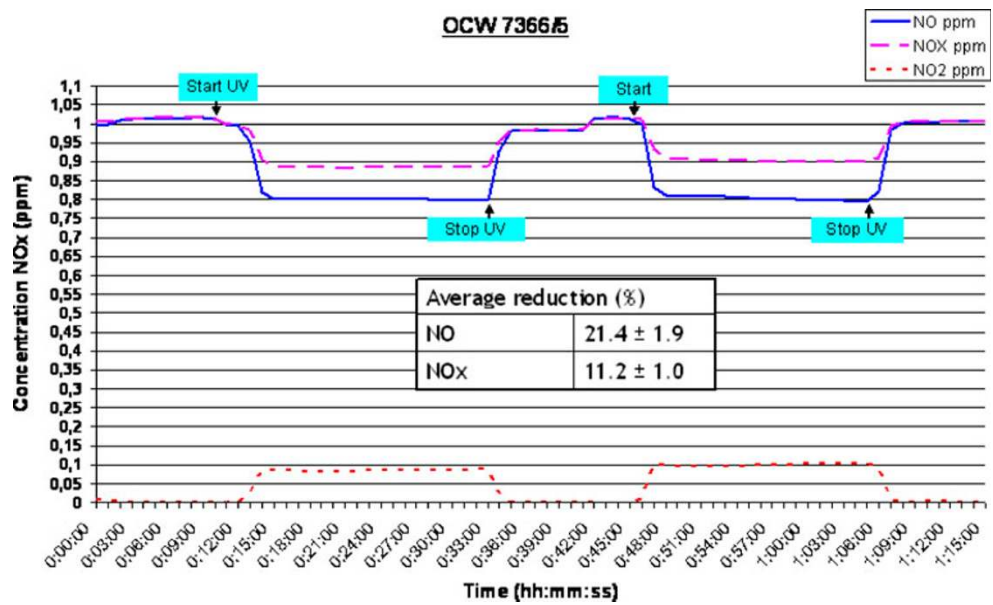


Fig. 13 Photocatalytic efficiency obtained for test plates of trial section in Wijnegem (photocatalytic dispersion on the surface)



according to the ISO-norm. The results are depicted in Fig. 13 and clearly show substantial and repeatable photocatalytic efficiency for these first test materials.

In order to improve the air purifying performance, further testing was undertaken in the laboratory in which the effect of different, important factors was studied:

- Effect of different materials in the mass
- Effect of different dispersions on the surface
- Influence of curing compound
- Influence of curing and/or storing conditions
- Effect of surface finishing
- Simulation of durability

First of all, it appeared that different photocatalytic materials available on the market (for mixing in the mass as well as applying on the surface) can give drastically different results regarding their air purifying performance, as shown in Fig. 14. Here, three different products have been mixed in

the mass of the concrete (1=integrated in cement, 2=TiO₂ powder, 3=TiO₂ suspension).

A second important influencing factor is the curing compound, which is generally applied after exposing the aggregates at the surface, to protect the young concrete against desiccation. Time of applying, in case of denudation, is approximately 24 h after putting the concrete in place. Its effect is illustrated in Fig. 15.

Apparently, the curing compound will initially inhibit the photocatalytic reaction, most likely because it is shielding off the active components from the pollutants in the air. Consequently, it is probable that the curing must disappear from the surface (normally after 1–2 months open to traffic and weathering) before the TiO₂ will reach its optimal air purifying performance. In case of a TiO₂ spray, this also means that it is best to apply the photocatalytic dispersion some time after the curing compound to have the best effect. Further measurements “on site” (see below) are planned to

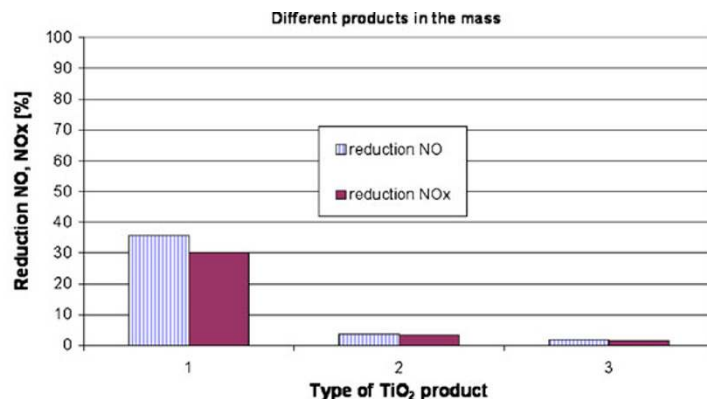
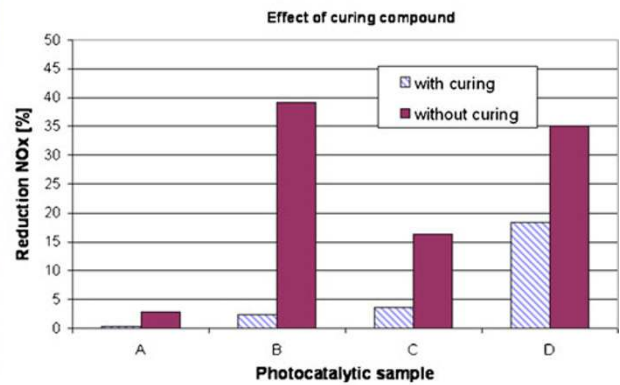


Fig. 14 Effect of different photocatalytic products (1=integrated in cement, 2=TiO₂ powder and 3=TiO₂ suspension) mixed in the mass of the concrete (no curing compound, modified curing procedure)

Fig. 15 Effect of curing compound on photocatalytic efficiency (different samples a–d, mass and/or dispersion, with and without curing)



reveal the short and long term effect of the curing compound on the photocatalytic performance.

Besides the curing compound, also the storage and curing conditions of the concrete play a role, although to a lesser extent compared to the former. The effect is most pronounced in the case of absence of a curing compound, where it can be seen that more humid conditions have an adverse effect on the photocatalytic efficiency. This is related to the relative humidity conditions at the surface of the concrete and the competition effect between water and pollutants as described above. Moreover, the hardening process of the concrete will slightly differ depending on the curing conditions which could in turn affect the porosity of the surface and hence, also the

photocatalytic action. This could be important in practice, because it is obviously hard to control these hardening conditions in situ.

To see the effect of surface treatment and more specifically of the exposed aggregates surface finish, a comparison among three different types of surface has been made (for one type of product): exposed aggregates, smooth (formwork side) and sawn surface. The results are depicted in Fig. 16. This shows that the exposed aggregates surface performs equally well as the smooth, formwork surface, but not as good as a sawn surface. This is the result of the combined action of less “active” cement at the surface and a higher surface porosity, two competing effects which in the end yield the final efficiency shown in Fig. 16.

Fig. 16 Effect of surface treatment on photocatalytic efficiency (only one type of “less” active product in mass)

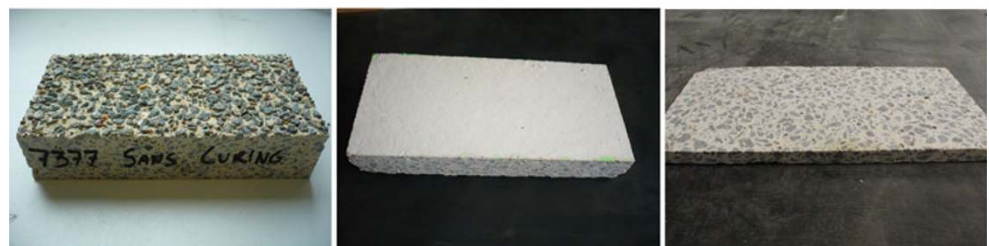
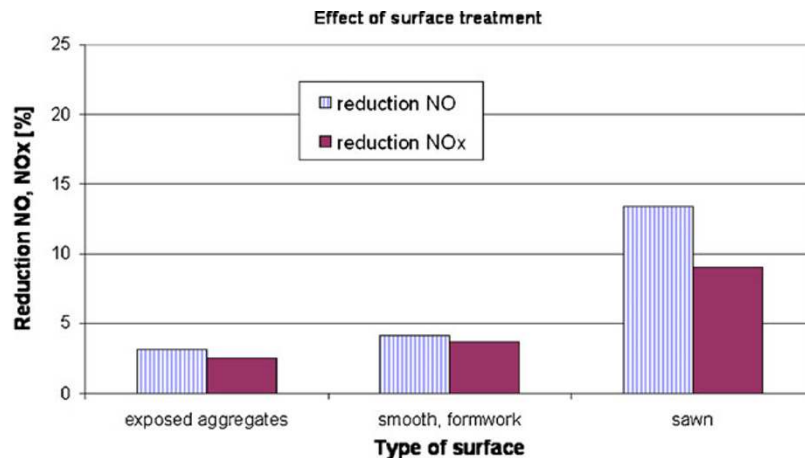
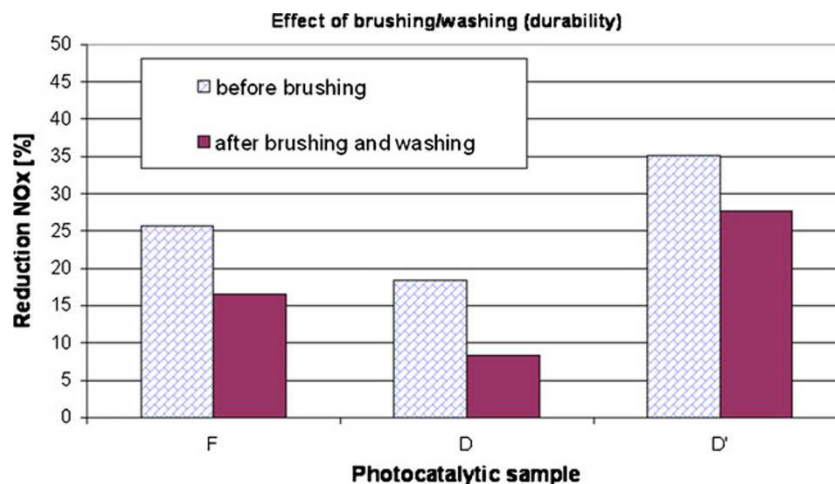


Fig. 17 Effect of brushing and washing the samples in the lab (simulation of durability)



Finally, the durability of the photocatalytic action was also tested in laboratory by simulating the possible effect of traffic and/or weathering on the surface, through brushing and washing of the samples. The influence of this action is illustrated in Fig. 17, where F, D and D' correspond to different types of photocatalytic samples (mass and/or dispersion, with or without curing).

The photocatalytic efficiency decreases by about 10 % after the brushing/washing operation. This demonstrates once again the need to assess the durability of these photocatalytic materials in situ and to check to longevity of the action after several years of service life.

In conclusion, the effect of the curing compound, curing conditions and surface finish has been clearly clarified, as well as the durability of the photocatalytic action in the lab. Based on these results and the optimization of the concrete composition, a proper selection of photocatalytic materials and of application procedures could be made, for the construction of double layered, photocatalytic concrete roads on the industrial zone “Den Hoek 3” in Wijnegem. A final choice has been made for the use of TiO₂ integrated in the cement, plus afterwards a surface application of a TiO₂ suspension, to be able to evaluate both types of applications and their durability.

Part of the road has been treated with curing compound; part of the road was covered with a plastic shield in order to prevent dehydration of the concrete during the first days. By this, the influence of the curing compound on the short term and long term photocatalytic efficiency can be investigated. In a later stage, a TiO₂ dispersion will also be sprayed on the surface. Furthermore, provisional controls of the photocatalytic efficiency in the lab and in situ, are carried out to check the separate action of the two types of photoactive materials (mass and dispersion), and to assess the durability of the air purifying performance. The construction works started in March 2011, after which the photocatalytic efficiency is/was followed in time (2011–2012), as demonstrated in Fig. 18. The first, preliminary results are very promising for now, but of course these have to be validated further on, also in order to see the influence of ageing, traffic and/or weathering on the photocatalytic efficiency in time.

6 Conclusions and perspectives

The use of photocatalytic pavement materials in order to minimize the air pollution by traffic is applied more frequently on site in horizontal as well as in vertical applications, also in

Fig. 18 Left: Construction of double layered, photocatalytic concrete road at industrial zone “Den Hoek 3” in March 2011; right: “On site” testing of photocatalytic efficiency



Belgium. Laboratory results indicate a good efficiency towards the abatement of NO_x in the air by using photocatalytic materials. Also, the durability of the photocatalytic action remains intact. However, the relative humidity is an important parameter which may reduce the efficiency on site. If the RH is (too) high, the water will be adsorbed at the surface and prevent the reaction with the pollutants.

Measurements on site in the past indicated a decrease of the pollution peaks due to the presence of the photocatalyst. Repeated measurements in the laboratory on photocatalytic concrete pavement blocks confirm the efficiency over time, even after more than 5 years of service life. Although a reduction in efficiency is evident due to the deposition of nitrate on the surface, the original efficiency can be regained by washing the surface.

The translation from the laboratory results to the “real” site efficiency is still a difficult factor, because of the great number of parameters involved. Hence, there is still a need for large scale projects to demonstrate the effectiveness of photocatalytic materials on site, including also other positive effects (O₃, VOC’s, PM...). To this purpose, two recent applications have also been started up in Belgium, which show already some very promising results. Here, the influence of several parameters (curing compound, surface finish, weathering conditions) affecting the photocatalytic activity in a practical case of road construction has been assessed to guarantee an optimal implementation. Furthermore, the best results will be achieved by modeling the environment, validating the model by measurements and implementing the different parameters to assess the real life effect (e.g. [18]). One must bear in mind that photocatalytic applications are only effective in case of good contact between pollutants and the active surface. Parameters as wind, street configuration and pollution source play an important role.

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