An environmental friendly solution for air purification and self-cleaning effect: the application of TIO_2 as photocatalyst in concrete

Anne BEELDENS
Researcher
Belgian Road Research Centre
Brussels, Belgium
a.beeldens@brrc.be

Abstract

Heterogeneous photocatalysis is a rapidly developing field in environmental engineering. It has a great potential to cope with the increasing pollution by traffic. The addition of a photocatalyst to ordinary building materials such as concrete, creates environmental friendly materials by which air pollution or pollution of the surface itself can be diminished.

TiO_2 is added to a cement mortar in order to diminish the air polluting effect by exhaust gasses. In particular, the conversion of NO_x to NO_3^- is measured. A detailed study of the principles of photocatalysis and of the interaction between TiO_2 and concrete is carried out. The laboratory study pointed at the influence of different parameters, such as temperature, relative humidity, light intensity, applied surface, material characteristics and flow rate. An upscaling of the test set-up has been carried out to see the influence of an increase in photocatalytic active surface.

In a more global approach, the application of TiO_2 as air purifying material is studied to be implemented in the urban and interurban streets and roads. In the European project NR2C, photocatalytic materials and different application methods are studied.

This paper presents an overview of the principle of photocatalysis and the application in combination with cement, as well as the results of the laboratory research, especially towards air purifying action. The implementation of this type of material in an urban and interurban area is discussed. A large scale realization with concrete pavement blocks is accomplished on the main roads (Leien) in the centre of Antwerp. An overview of this realization is given.

Keywords: TiO_2; photocatalysis; air purification; surface treatment

1. Introduction

“Quality of life” is becoming a main issue in modern urban environments. Comfort, mobility, energy resources and respect for the environment are key points of interest in future developments. In the European project NR2C (New Road Construction Concepts), new developments and technical innovations are looked at and integrated in a global vision of the road of the future. The adaptation of the surface transport infrastructure in European countries to new societal and environmental demands is a major objective for the project.

Following the expression and derivation of new concepts for the roads of the future from a global perspective, a number of targeted innovations of special interest are developed. The application of TiO_2 at the surface of concrete pavement blocks is one innovation, which replies to the social demand of safe, comfortable and environmental friendly road surface infrastructures.

2. Heterogeneous photocatalysis, a process for air purification

2.1. Air pollution by traffic exhaust

A variety of air pollutants have known or suspected harmful effects on human health and environment. In most areas of Europe, these pollutants are principally the products of combustion from space heating, power generation or from motor vehicle traffic. Pollutants from these sources may not only prove a problem in the immediate vicinity of these sources but can travel long distances, chemically reacting in the atmosphere to produce secondary pollutants such as acid rain or ozone.
The principle pollutants emitted by vehicles are carbon monoxide, oxides of nitrogen (NO_x), volatile organic compounds (VOC's) and particulates. These pollutants have an increasing impact on the urban air quality. In addition, photochemical reactions resulting from the action of sunlight on NO_2 and VOC's lead to the formation of 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 NO_3 and finally precipitation of nitrogen acid with harmful consequences for building materials (corrosion of the surface) and vegetation.

2.2. Heterogeneous photocatalysis

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, photocatalytic materials can be added to the surface of pavement and building materials. In combination with light, the pollutants are oxidized, due to the presence of the photocatalyst and precipitated on the surface of the material. Consequently, they are removed from the surface by the rain.

Heterogeneous photocatalysis with TiO_2 as catalyst is a rapidly developing field in environmental engineering. It has a great potential to cope with the increasing pollution. The impulse of the use of TiO_2 as photocatalyst was given by Fujishima and Honda in 1972 (Fujishima and Honda 1972). 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 decomposed by adding TiO_2 under influence of UV-light. The application of TiO_2 as air purifier originated in Japan in 1996. A broad spectrum of products appeared on the market for indoor use as well as for outdoor use.

Heterogeneous photocatalysis with TiO_2 as catalyst results in a total mineralization of a broad gamma of organic compounds (alkanes, alkenes, alcohol, pesticides,…) Further, it is possible to reduce NO_x, bacteria, viruses,… The speed at which these reactions take place depends on the intensity of the light, the environmental conditions (temperature, relative humidity), the amount of TiO_2 present at the surface and the adhesion of the pollutants to the surface. In the case of traffic, it is important that the exhaust gasses stay in contact with the surface during a certain period. The geometrical situation, the speed of the traffic, the speed and direction of the wind, the temperature, influence the final reduction rate of pollutants in situ.

2.3. TiO_2 and the photocatalytic process

TiO_2 is a metal, which is multiply present in nature. The oxygen TiO_2 has three different molecule structures: rutile, anatase and brookiet (Fujishima et al. 1999). Rutile is known as pigment in white paints, but shows up till now low photocatalytic reactivity. Anatase is preferable if used as photocatalytic cell. To use anatase in heterogenic photocatalysis, UV-light with a wave length lower than 387 mm has to be present. Also the intensity of the light is important to optimize the photocatalytic activity. Normal daylight can be used for the photocatalytic reaction. Research is focusing now on the application of nano-particles of TiO_2, active in the visible light range.

Existing applications may be found in water purification, air conditioning (air purification), self-cleaning glazing, ceramic tiles (self-cleaning, antibacterial,…), textile (anti-odour), mirrors (anti-condensation), tunnel lightning, white tents,… Besides the air purifying and antiseptical action, where the pollutants are oxidized or reduced due to the presence of the photocatalyst, TiO_2 is also used to obtain a self-cleaning material. This is due to a very high hydrophilicity of the surface when TiO_2 is activated by UV-light. The water layer is attracted between the dirt and the surface resulting in the washing off of the dirt particles. This effect is more pronounced with smooth surfaces like glass and ceramic tiles. In the case of concrete surfaces, the self-cleaning effect will be more limited due to the physical anchoring of the dirt in the larger pores. In addition, due to photocatalytic working, a decomposition of the dirt particles, especially of the organic particles takes place, followed by the washing of the surface resulting in a cleaner surface.

2.4. Application of TiO_2 in building materials as photocatalyst

The increase in patents during the last decade indicates a huge interest, especially from Japan and Europe, in the application of TiO_2 as photocatalyst in building materials. Regarding the reduction of air pollution due to traffic in urban areas, the application on pavement surfaces or on the building surfaces in cementitious materials gives optimal solutions. To increase the efficiency of the photocatalyst, its presence at the surface of the material is crucial. It has to be accessible by sunlight to be activated. Consequently, the pollutant has to be absorbed on the surface and oxidized or reduced to a less harmful element.

The goal is to have as much TiO_2 as possible at the surface of the material, without the risk of loosing it by abrasion or weathering. Up till now, the most efficient way to apply the TiO_2 is in a thin layer cementitious material, which is placed on the surface. Application in concrete tiles is therefore very suitable: the TiO_2 can be added to the weathering layer. If the layer is slightly used, new TiO_2-particles will be present at the surface.
Other applications can be found in architectural concrete. The use of white cement with TiO_2 at the surface of buildings and construction attribute to the durability of the visual aspect of the building. Due to the photocatalytic action, the whiteness of the building will remain and dirt will be washed away more easily due to the hydrophilic properties or will be decomposed. The application of photocatalytic panels at the facades of buildings is investigated in the European PICADA project (Maggos et al. 2005).

3. Laboratory results: parameter evaluation

To determine the air purifying activity of TiO_2, applied in building materials, the oxidation of NO and NO_2 into NO_3 is determined. Emphasis is put on this pollutant, since it is one of the most important pollutant produced by traffic and plays a major role in the formation of smog and ozone. It is also one of the pollutants on which limits have been places by the Kyoto agreement. The oxidation of the NO is simplified presented by the following equations:

$$NO + {}^{\bullet}OH \xrightarrow{h\nu,\, TiO_2} NO_2 + H^+$$

$$NO_2 + {}^{\bullet}OH \xrightarrow{h\nu,\, TiO_2} NO_3^- + H^+$$

Other parameters which are important is the relative humidity and the temperature. At higher temperatures, the conversion will be better. The relative humidity is important, since the water in the atmosphere plays a role in the adhesion of the pollutants at the surface and therefore also the conversion rate. In the case of a higher relative humidity, the conversion will be lower. Optimal conditions are therefore reached on hot summer days with high temperatures and low R.H.. It is also on those days that the risk on smog during the summer is the highest and thus the efficiency of the air purification is the highest.

The NO_3^-, which is formed during the process, will precipitate on the surface of the stone. To retain the efficiency of the material, the deposit will have to be washed away by rain or by cleaning the surface with water.

3.1. Test set-up

The test set-up is based on the Japanese standard JIS TR Z 0018 “Photocatalytic materials –Air purification test procedure”, which is also adapted in a proposal for an ISO standard (2/2/2004): “Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for air purification performance of photocatalytic materials – Part 1: Removal of nitric oxide”, ISO TC 206/SC N. The test set-up consists of a metal container, in which 1 pavement block is placed, with a UV-transparent glass at the top. Air with a NO-concentration of 1 ppm is blown over the surface with a flow rate of 3 l/min. The height of the free space is 3 mm. The temperature is approximately 23°C and the relative humidity is 50%. The light intensity is equal to 10 W/m² in the range between 300 and 460 nm. The maximum is at 365 nm. The set-up is illustrated in figure 1.

*Fig. 1 Set-up of the test to determine the air purifying properties with large container (3*2 rows of pavement blocks)*

The concentration of NO and NO_2 is measured at the outlet of the container. The test is executed during 5 hours. 30 minutes prior to the test, the concentration of the air is measured without illumination to ensure that there is no deposit of the NO on the surface.

3.2. Results

A typical result of the test is given in figure 2. The inlet concentration is equal to 1 ppm. As soon as the light is put on, the concentration drops with approximately 40%. After 5 hours of illumination, the NO is cut off for 30 min. Consequently, the light is put off again and the NO is concentration is measured. The results indicate a small increase in NO_2, but a significant decrease in NO_x ($NO+NO_2$). The final decrease depends on the material itself, on the size of the surface exposed, on the concentration of NO, on the light intensity, the ambient temperature and the flow rate.

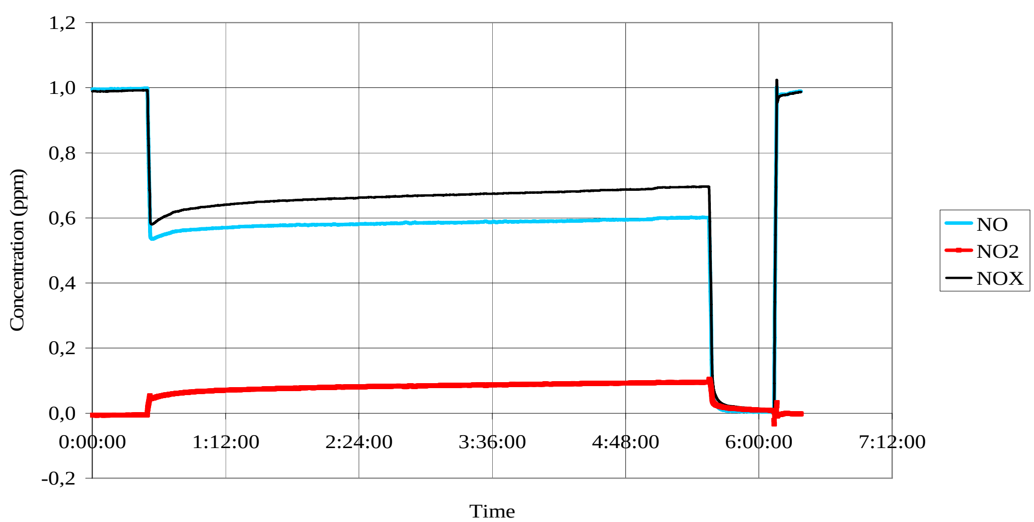

Fig. 2 Results obtained in laboratory according to the standard test procedure

By increasing the surface by 6 (2 rows of 3 pavement blocks) for instance, a further reduction is obtained (up till 85%), which results in a NO_x concentration of 13.5% at the outlet, as can be seen in figure 3. This is very promising for the extrapolation to the situation in situ. By increasing the time of contact or increasing the surface over which the air flows, the reduction will be even more significant.

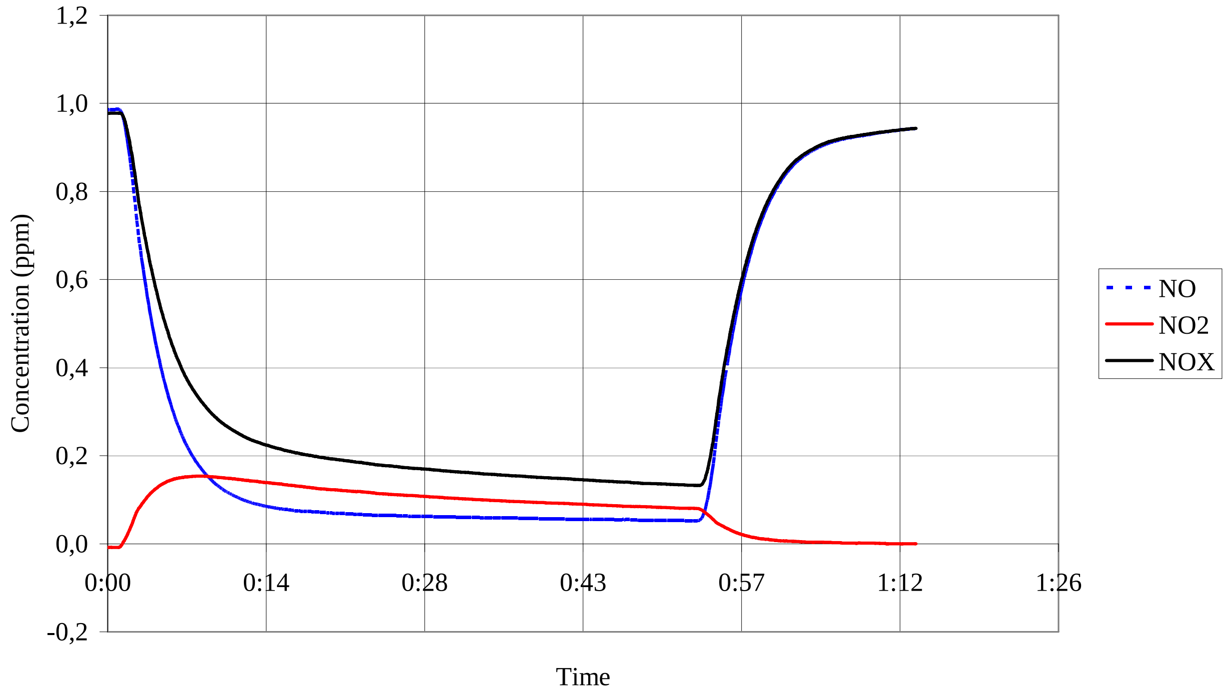

Fig. 3 Results obtained on a larger surface of photocatalytic pavement blocks

4. Pilot project in Antwerp

An important issue is the conversion of the results, obtained in the laboratory to real applications. The construction of a test section of 10.000 m² photocatalytic pavement blocks as pilot project on the parking lanes of a main axe in Antwerp allows us to search for answers on frequently asked question, like the amount of reduction of NO_x, the durability of the material not only for mechanical and aesthetical properties, but also for the photocatalytic efficiency, the minimum surface needed related to traffic density and the frequency of maintenance, i.e. washing off of the surface by rain or by artificial spraying.

Figure 4 gives a view of the parking lane, where the photocatalytic concrete pavement blocks are applied. Only the upper layer of the blocks contain TiO_2.

Fig. 4 Separate parking lanes at the Leien of Antwerp with photocatalytic pavement blocks

To obtain results towards the reduction of e.g. NO_x and on the durability of this reduction, different measurement techniques may be applied. The use of the global measurement sites is not appropriate, due to the limited surface covered by the photocatalytic pavement blocks, compared to the overall surface. Local continuous measurement of the NO and NO_2 concentration demands a long period during which the measurement has to be conducted, to eliminate the influence of parameters such as wind, temperature, light intensity, traffic intensity and so on. Although the presence of a reference lane allows comparing measurements, the time needed to come to reliable results will be too long. Another method, which seems to be more suitable, is the measurement of NO_3-deposite on the surface of the blocks. The NO and NO_2 which is oxidized into NO_3 is deposited on the surface. By washing off the stones with distilled water and determining the amount of N in the water, an idea of the minimum amount of reduced NO_x can be obtained. Furthermore, a regular measurement in the laboratory will be executed on blocks from the surface to measure the possible reduction of efficiency under controlled conditions.

First results indicate a reduction over time of the efficiency of air purification of 20% after 1 year. The measurements will continue over 2 more years to see the influence of aging, dirt, season,…

5. Conclusions and further research

This paper focuses on the application of TiO_2 as photocatalytic material in concrete pavement blocks. The addition of TiO_2 in building materials adds an additional property to the road. Purification of the air, which is in contact with the surface, is obtained when the surface is exposed to UV-light (present in daylight).

The measurements in the laboratory on photocatalytic pavement blocks gave good results towards air purification, measured as NO_x reduction. The best results were obtained by high temperature (> 25°C), low relative humidity, high light intensities and long contact times. This situation is obtained on hot sunny days, without any wind, when the risk on smog formation due to the high rate of pollution is the biggest.

A pilot project of 10.000 m² is constructed in Antwerp. Measurements to reveal the air purifying efficiency in situ and the durability of this efficiency are programmed. A reduction of 20% of purification efficiency is measured after app. 1 year in service.

6. References

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7. Acknowledgements

The author wishes to thank IWT-Flanders for its support to this project. (VIS-CO 020790).