# Decontamination through Photocatalytic $TiO_2$ Additions - Past, Present and Future

Juan de Dios, Jose María del Campo, and David Colorado

***Abstract*—**The large industrial activity and the increased automotive fleet generate pollutants which result in a progressive deterioration of the environment. Pollution and air quality deterioration are the result of complex phenomena that derive from multiple causes and associated effects, and are usually due to human activities and to pollutants emitted into the atmosphere.

Cities are exposed to high levels of pollution which cause a negative impact on human health. The pollutants which currently seem to be pose more serious health hazards, both in Spain and in the European Union, are particulate matter, nitrogen oxides, and tropospheric ozone.

Research advances into the effect of certain pollutants, implementation of stricter environmental standards, and economic factors have boosted the development of new technologies of purification. The strict environmental regulations that have been established by the Administrations have stimulated research into development of new strategies of atmospheric decontamination. Photocatalysis is an effective method for the treatment of a wide range of air and water pollutants. In particular, certain semiconducting materials, such as $TiO_2$, have demonstrated to have a high efficiency of degradation of organic compounds.

This paper analyzes the addition of different crystalline phases of this material, as well as several real scale application cases in civil works and edification. It concludes with some questions yet to be studied as well as some futures lines of research.

***Keywords*—**Nitrogen oxides ($NO_x$), photocatalysis, photocatalytic efficiency, titanium dioxide ($TiO_2$).

## I. Introduction

CURRENTLY atmospheric pollution poses serious health hazards to the public [1], since it is the cause of many premature deaths worldwide and contributes to a great number of chronic diseases [2], such as lung and cardiovascular diseases. The adverse effects on human health cannot be attributed to a single pollutant, but rather to a mixture of many pollutants in the atmosphere.

Quality air deterioration is the result of phenomena whose origin resides mainly in human activities [3]. Traffic flow is one of the main sources of pollutant emission, not only because of the burning of fossil fuels, but also because of the wear of components of automobiles, including brakes, tyres, and the firm layer on which they tread [4]. Another major cause of atmospheric pollution is the emission of gases generated in industrial activities. Among the most hazardous contaminants on human health, nitrogen oxides ($NO_x$), particulate matter (PM), and tropospheric ozone ($O_3$) stand out [5], [6].

The main source of nitric oxide (NO) and nitrogen dioxide ($NO_2$), commonly known as nitrogen oxides ($NO_x$), is the combustion of fossil fuels. Nitrogen oxides ($NO_x$) also have a negative effect on water and land quality because they contribute to the formation of acid rain and because nitrogen dioxide favors the formation of tropospheric ozone and particulate aerosols.

Regardless of the increase of environmental regulations on atmospheric emissions (Directive 2010/75/UE) and of the current established limit values on air pollution [7], which emphasize on nitrogen oxides ($NO_x$) released primarily by diesel engines and with which emission and effects of pollutants have been tried to be mitigated, it is clear that corrective measures that have been taken so far [3], such as ventilation systems and filtrating devices in industrial chimneys, are not sufficient.

The present paper studies the photocatalytic oxidation [8] of nitrogen oxides ($NO_x$) as a solution to counteract pollution. Photocatalysis can remove not only nitrogen oxides ($NO_x$) but a wide range of other contaminants as well [9], including sulfur oxides, volatile organic compounds, and even carbon monoxide. The photocatalysis process stems from the decontamination principle of nature and consists of a photochemical reaction in which solar energy is converted into chemical energy at the surface of a semiconducting catalyst, which accelerates the rate of reaction by means of its semiconducting nature.

The photocatalytic oxidation of nitrogen oxides ($NO_x$) to nitrates ($NO_3^-$) [10] produces a series of reaction products in low concentration in the form of nitrate anions that can be then removed from the atmosphere by rainfall water [11].

Many semiconducting materials have photocatalytic activity, e.g., ZnO, $Fe_2O_3$, CdSe, CdS and $TiO_2$ [12]. $TiO_2$ is a convenient photocatalyst because it has low toxicity, compatibility with diverse construction materials, high photocatalytic activity, and high chemical stability under light irradiation [13]. In addition, it is relatively inexpensive compared to other photocatalytic semiconductors.

Juan de Dios is Marketing Manager for Spain in the construction firm OHL, Madrid, Spain. (corresponding author's phone: 0034680449639; e-mail: jdedios@ohl.es).

Jose María del Campo is Professor in the Department of Civil Engineering: Construction Technology of the Technical University of Madrid. Spain. (e-mail:josemaria.delcampo@upm.es).

David Colorado is Professor in the Department of Physics. Higher Polytechnic School. University Alfonso X El Sabio. Madrid. (e-mail: dcoloara@uax.es).

$TiO_2$ is compatible for addition into cement, one of the most traditionally used materials in construction, not affecting its basic properties [13]. Addition of $TiO_2$ into cement-based structures strategically placed in spots where pollution concentration is high can contribute to considerably reducing local levels of pollution.

## II. Methodology

In the 1970s numerous researchers began studying the photocatalytic effect of $TiO_2$. Laboratory scale tests showed that the radicals generated during the photocatalytic process were able to oxidize all the organic and inorganic species in the surrounding area. The photocatalytic effect thus offers the opportunity to reduce the concentration of pollutants, including toxic gases and unpleasant smells [14].

Catalysis can be defined as the acceleration of chemical reactions by a species, known as catalyst, which is not consumed by the reaction Fig 1 [14], [15]. There are two types of catalysis depending on the state in which the reactants are: in homogeneous catalysis, reactants exist in the same phase (e.g., liquid), whereas in heterogeneous catalysis reactants exist in different phases (e.g., liquid and solid). According to this definition, electromagnetic radiation cannot be considered a catalyst since the energy of photons is consumed during the reaction; instead, the concept of induced catalysis applies [16]. For semiconductors, band-gap is defined as the energy difference between the valence band (VB) that is completely occupied, and the conduction band, which is empty. The energy difference between the conduction band and the valence band is called forbidden band. A list of the most widely used photocatalysts and their optimal wavelengths and corresponding forbidden bands is shown in Table I [12].

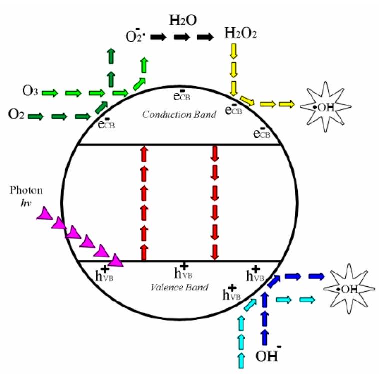


Fig. 1 Representation of the activation of the photocatalytic process

TABLE I
LIST OF DIFFERENT PHOTOCATALYSTS AND THEIR RESPECTIVE WAVELENGTHS AND FORBIDDEN BANDS

| Photocatalyst | Wavelength (nm) | Forbidden band (MV) |
|---|---|---|
| ZnO | 390 | 3,2 |
| CdSe | 730 | 1,7 |
| CdsS | 497 | 2,1 |
| $Fe_2O_3$ | 564 | 2,2 |
| $TiO_2$ | 390 | 3,0 |

The photocatalytic properties of $TiO_2$ are based on their optoelectronic properties. Because it is semiconducting, it can absorb photons that have the necessary energy required to transfer electrons from the valence band to the conduction band [15]. Absorbable photons are within the near ultraviolet (UV) region of the electromagnetic spectrum, and correspond to a band gap of 3.2 eV [16]. Titanium dioxide is a semiconductor that absorbs radiation in the visible-UV range (UV 315-380 nm and visible 380-780 nm). According to different authors, the crystalline anatase phase is at a gap of 3.2 eV corresponding to a wavelength of approximately 380 nm, whereas the crystalline rutile phase has a gap of 3.0 eV which corresponds to a wavelength of 413 nm. UV absorption creates electron-hole pairs that are responsible for the generation of radicals and charged species on the surface of $TiO_2$, as described in Fig 1 [14]. Thus $TiO_2$ becomes oxidative and is able to degrade organic molecules that precipitate at its surface. A reference of the great oxidizing potential of the generated species is the fact that oxidril radicals, formed in the photocatalytic reaction, are the most oxidizing radicals after fluoride radicals.

The reactions that take place in the process are [17]:

$$TiO_2 \rightarrow^{hv} TiO_2(h_{vb} + +e_{eb}{}^{-}) \quad (1)$$

$$h_{vb}{}^{+} + OH^{-} \rightarrow HO^{+} \quad (2)$$

$$e_{vb}{}^{-} + O_2 \rightarrow O^{-}{}_2 \quad (3)$$

$$2O_2 \rightarrow H_2O_2 + 0_2 \quad (4)$$

$$H_2O_2 + e_{eb}{}^{-} \rightarrow HO^{\cdot} + OH^{-} \quad (5)$$

Where:
$e_{eb}^-$ is an electron in the valence band
$h_{vb}^+$ is a hole in the valence band

The five parameters which have the greatest influence on the rate of reaction of photocatalysis of $TiO_2$ are: a) Mass of photocatalysis, b) Wavelength, c) Contaminant concentration, d) Temperature, and 2) Radiation flux ($W/m^2$).

Fig. 2 shows the influence of each of these parameters, from where the following is observed [18]:

a) Mass of catalysis (Fig. 2a): Decontaminating efficiency increases proportionally with the amount of surface covered by $TiO_2$ and with the thickness of the layer used until a maximum level is reached that coincides with a plateau in photocatalytic activity, i.e. a constant, maximum level of photocatalysis is reached at high mass of catalysis.

b) Wavelength λ: Photocatalytic activity is parallel to radiation wavelength, i.e., it can only be produced under light radiation of the appropriate wavelength for each semiconductor.

c) Contaminant concentration (Fig. 2c): For gaseous, aqueous, and precipitated solid contaminants, photocatalytic activity varies as a function of partial pressure or concentration according to a Langmuir-Hinshelwood type heterogeneous reaction, in which the rate of reaction of photocatalytic degradation is proportional to the concentration of decontaminant.

http://dx.doi.org/10.15242/IIE.E0514557

d) Temperature: The influence of temperature on the rate of photocatalytic reaction is conventionally fitted to the Arrhenius' function with the following equation (6) [18], [19]:

$$\log r = f\left(\frac{1}{T}\right) \quad (6)$$

Which is obtained by linear transformation of the Arrhenius' equation (7):

$$r = r_0 \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (7)$$

Where:

- $r_0$ is the pre-exponential factor.
- T is the absolute temperature.
- R is the universal gas constant.
- $E_a$ is the activation energy, which is calculated from the slope of the linear transformed equation.

The Arrhenius' curve shows three different behaviors (Fig. 2d). The central part corresponds to ambient temperatures and has a small slope, corresponding to a low activation energy and to a small effect of temperature on photocatalytic rate, which makes the photocatalytic effect an ideal application under ambient conditions.

e) Radiation flux (φ): Its influence depends on its value. When $\varphi \leq 25$ mW/cm$^2$, the rate of reaction increases proportionally with φ; this is associated with a good photocatalytic behavior. When $\varphi \geq 25$ mW/cm$^2$, photocatalytic activity increases with the square root of φ [18].

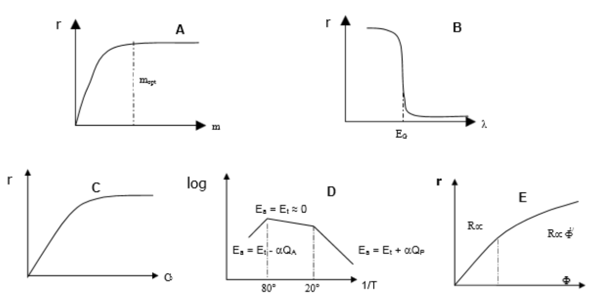


Fig. 2 Effect of different parameters on the rate of photocatalytic reaction produced by UV radiation of $TiO_2$

*A. Decontamination by addition of titanium dioxide to cementitious materials*

The process of decontamination by addition of $TiO_2$ into cementitious materials begins with the generation of radicals at the surface of $TiO_2$ under UV-Vis irradiation. Fig. 3 illustrates a simplified mechanism of degradation of nitrogen oxides by photocatalysis and their removal from the atmosphere with the product TioCem®. $NO_x$ from the atmosphere reaches the generated radicals on the surface of a cement-based material, producing nitric acid, which reacts with calcium carbonate, a constituent of cement, to form calcium nitrate, and releases $CO_2$ and water into the atmosphere.

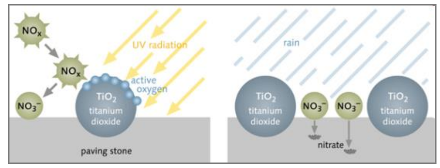


Fig. 3 Simplified mechanism of the degradation of nitrogen oxides by photocatalysis

The synergy created by the addition of $TiO_2$ to a cementitious substrate [20] produces a $TiO_2$-cement composite ideal for application under ambient conditions. Many photo-oxidizable compounds, such as $NO_2$ and $SO_2$, are acid. Therefore, the cementitious matrix, which is alkaline, is an ideal substrate to fix the catalyst, pollutants, and photocatalytic reaction products. Another key factor is the specific surface area of the catalyst; the larger it is the greater the photocatalytic activity of the combined $TiO_2$-cement system is.

The use of photocatalytic cement-based materials enables breaking nitrogen oxides down to nitrates on the surface of the cementitious matrix. The nitrates precipitated on the surface are dissolved with rainfall water, draining down the sewers in a simple and natural process of removal [21].

Since nitrogen oxide degradation by photocatalytic products requires solar energy, photocatalytic efficiency is evaluated with the following formula (7) [33]:

$$NO_{oxidation\text{-}rate} = \frac{P}{R \cdot T} \cdot \frac{Q}{A} . (C_{UVof} f - C_{UVon}) \quad (8)$$

Where:

P: Atmospheric pressure expressed in atmospheres (atm) $C_{UVOff}$

R: Universal gas constant $\frac{J}{atm \cdot K}$.

Q: Volumetric flow rate

A: Surface area

$C_{UVoff}$: NO Concentration without light irradiation

$C_{UVon}$: NO Concentration under light irradiation

$TiO_2$ participates as an intermediary in NOx decomposition without being consumed in the reaction. Rainfall water or an alternate cleaning system with water serve to wash the surface of $TiO_2$, thereby restoring its original efficiency [**Error! Bookmark not defined.**].

The photocatalytic activity of $TiO_2$ in anatase crystalline phase cannot only degrade nitrogen oxides but can also reduce the concentration in air of volatile organic compounds (VOC) and particulate matter ($PM_x$) [23].

*B. Decomposition of nitrogen oxides*

The decomposition of nitrogen oxides is known as $DeNO_x$ (9), (10) process and consists of a two-step reaction that usually takes place on the surface of the photocatalyzing material [22]:

$$NO + OH^{\cdot} \rightarrow NO_2 + H^+ \quad (9)$$

$$NO_2 + H^{\cdot} \rightarrow NO_3^- + H^+ \quad (10)$$

Where hydroxyle free radicals ($OH^{\cdot}$) originate at the surface of $TiO_2$ - anatase in the presence of water under UV light radiation. OH· radicals have a strong oxidizing power and thus they oxidize NO to $NO_2$ in the first reaction step. The generated $NO_2$ is then oxidized to nitrate ion ($NO_3^-$), which can bond to dissolved alkali in the cementitious matrix or, even more likely, they can be removed from the concrete surface as weak nitric acid [23].

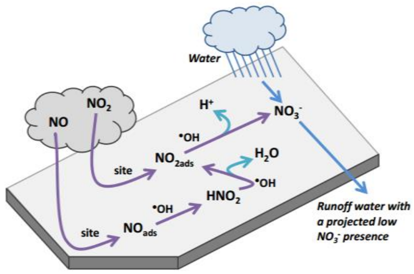


Fig. 4 Illustration of the mechanism of photocatalytic oxidation for concrete pavement containing $TiO_2$

## III. Applications

Market sectors that currently incorporate photocatalytic products comprise a diverse range and include the construction, automobile, environment, energy, and medical sectors. A more exhaustive analysis within the construction industry indicates that the application of photocatalytic products focuses on both outdoor and indoor settings. Self-cleaning paint and glass for indoor settings have been commercialized, but current and future markets focus on research into applications aimed at reducing pollution and at improving environmental quality, without neglecting the basic properties, minimum required strengths and inherent characteristics of the construction material [24].

According to the European Photocatalysis Federation, practical application of photocatalytic construction materials is expected to increase annually by up to 15%, with the most pronounced increases occurring in Asia and Europe (Fig. 5) [22], [24].

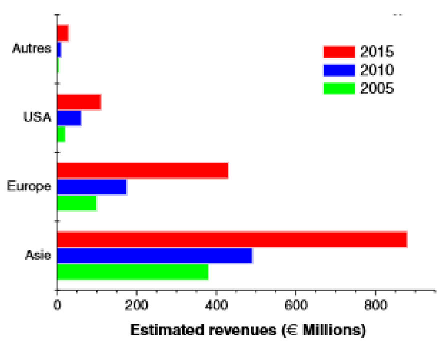


Fig. 5 Market sectors and geographic markets of photocatalytic products

## IV. Real Scale Applications

Table II shows a list of the measured photocatalytic efficiency of different products applicable for roads and concrete and distributed by different companies. These practical applications are placed in areas where pollution concentration due to automobile gas exhaust is high.

As it is observed in Table 2, the efficiency of photocatalytic products applied in areas where pollution is high varies from 15 to 60%.

The following construction works have been analyzed: Crematory of South Madrid Cemetery, Loyola Church in San Sebastian, the street Jean Bleuzen in Vanves (France), the road pavement in Segrate, Milan, the tunnel within road Porpora, also in Milan, the stoned pavement in Calusco, in Bergamo, Italy, the street Borgo Palazzo in Bergamo, Italy, and the tunnel Umberto I in Rome, among others.

Table II shows a summary of the $NO_x$ reductions achieved by addition of $TiO_2$ in the construction works.

### *A. Pavement Ecopeco®. Incinerator in South Madrid Cemetery*

Incinerator in South Madrid Cemetery. An Ecopeco® pavement with a surface area of 6,500 $m^2$ has been used, causing a $NO_x$ reduction equivalent to the daily combustion of 2000 automobiles. The cement used for cobble/paving stones, TX Active®, has photocatalytic properties that help actively to reduce concentration of $NO_x$, $SO_x$, ozone, and dioxins, among other compounds harmful for human health and for the environment [25], [26].

### *B. Loyola Crunch, San Sebastian*

The new church designed by architect Rafeel Moneo in Donostia, San Sebastian, and consecrated on 14 May, 2011, has maintained its white walls intact and clean a year after it was constructed, thanks to Tx Aria®, a novel morter application based on the technology TX Active®, patented by FYM-Cementos Rezola, a firm of the group Italcementi, with the aim of fighting urban pollution [30].

Fig. 6 Loyola Crunch, San Sebastian [30]

### *C. L Street Jean Bleuzen, Vanves, France*

The street Jean Bleuzen is considered a “Street canyon”, i.e., a relatively narrow street with buildings on both sides, perpendicular to the strongest winds of the area and exposed to high solar radiation. It is has an esteemed IMD of 13,000 automobiles per day. During the Reevalution Plan of Vanves, concrete incorporating TX Aria ® was used to build a length of 300 m, which involves a surface area of about 6.000 $m^2$ accounting for sidewalks, kerbs, and the road [32]. According to monitoring reports of the area, not only there was a 20% reduction in gas pollution but acoustic pollution decreased as well.

TABLE II
LIST OF REAL PHOTOCATALYTIC APPLICATIONS IN THE CONSTRUCTION SECTOR AND CORRESPONDING POLLUTANT REDUCTION

| Location | Date of completion | Treated Surface | Contaminant/ $NO_x$ reduction | Installation Type | Pavement Type | Traffic volume |
|---|---|---|---|---|---|---|
| Crematory of South Madrid Cemetery [**Error! Bookmark not defined.**] | 2013 | 6,500 $m^2$ | | - | Cement TX Active® | - |
| Loyola Church, San Sebastian [**Error! Bookmark not defined.**] | 2011 | 10,500 $m^2$ | | - | TX Aria® | - |
| Jean Bleuzen Street, Vanves, Francia [**Error! Bookmark not defined.**] | | 6.000 $m^2$ | 20% | Urban | Paving blocks TX Aria ® | 13,000 auto/day |
| Road pavement in Segrate, Milán [**Error! Bookmark not defined.**] | 2002 | 7.000 $m^2$ | 60%. | Urban road | Thin mortar overlay TX® | 1000 auto/ hr. |
| Road within tunnel Porpora, Milán [**Error! Bookmark not defined.**] | 2006 | - | 22,7 % | Road within tunnel | Concrete photocatalytic ceiling paint TX Aria® | 30.000 auto/day |
| Stoned pavement in Calusco, Bergamo, Italy [**Error! Bookmark not defined.**] | 2003 | 8.000 $m^2$ | 45% | Industrial road | Paving blocks TX Aria® | - |
| Street Borgo Palazzo, Bergamo, Italy [**Error! Bookmark not defined.**]. | 2006 | 7.000 $m^2$ | Height from groundfloor / $NO_x$ / NO | Urban | Paving blocks TX Aria®. | 400 auto/hr. |
| | 2007 | | 30 cm / 30% / 33% | | | |
| | | | 180 cm / 20% / 20% | | | |
| Tunnel Umberto I, Rome [**Error! Bookmark not defined.**]. | 2007 | 9.000 $m^2$ | $NO_2$ / NO | - | TX Aria®. | |
| | | | 19% / 25% | | | |
| Urban road in St. Denis, France [25] | - | 2.000 $m^2$ | 40-50 % | Urban road | Concrete overlay | |
| Castorweg Street in Hengelo, The Netherlands [26] | 2013 | 750 $m^2$ | 19-45% | Urban road | Paving blocks and spray coating | 110 auot/hr. |
| Parking garage in Milan, Italy [27] | | 4.000 $m^2$ | - | Parking garage | Spray coating on asphalt | - |
| Multiple locations in sidewalks and urban roads in Japan [28] | 2011 | 25.000 $m^2$ | - | - | - | - |
| Parking lanes of urban road in Antwerp, Balgium [29] | | 10.000 $m^2$ | 20% | Parking lanes of urban road | Paving blocks | - |

### D. Road pavement in Segrate, Milan

In November 2002 the efficiency of photoactive binders in reducing $NO_x$ by their addition into a horizontal structure was demonstrated in Via Morandi, in the municipality of Segrate, Milan [27].

Via Morandi is a double way street with a width of 10 meters. It has trees on both sidewalks, parking areas, and buildings on both sides at distances between 7 and 10 meters to the edges of the street. There is also a 30 meter wide central opening between two building, and properties are separated between them by fences, preventing air circulation. The street has an IMH higher than 1000 automobiles per hour and the characteristics of the street are practically constant along the entire layout where testing was performed, all of which made this spot ideal for testing [28].

The experiment was carried out on an area of 7000 $m^2$, on a stretch from the junction of Via Modigliano up to past the intersection of Via Turati, with a length of 230 m. A thin layer of mortar with photoactive hydraulic base TX® was applied onto the bituminous-based pavement; and a loxometer, a hot-blade anemometer, a *Nitrogen Oxides Analyzer*, and a Data Logger were used for test analysis [16]. After monitoring the area, an approximate $NO_x$ reduction of 60% was observed [32].

Fig. 7 Placement under photocatalytic mortar

### E. Tunnel of Via Porporea

The tunnel of Via Porporea, located in Milan, is 104 meter long and 7 meter wide. It is located near the station Lambrate in Milan and connects Via Propora with Piazza Monte Titano. The tunnel has two-way traffic and is placed along a first-category arterial axis that connects the center of Milan with the bypass road, which presents an IMD of up to 30,000 automobiles per day [32]. Traffic measurements were carried out by the mobility and environment agency with the support of the municipal police. Photocatalytic materials were used to rehabilitate the tunnel. The company Italcementi used a pavement for high performance concrete roads, where the concrete was made from grey cement TX Aria® [30]. Monitoring and data processing campaigns carried out by ARPA Lombardy showed a $NO_x$ reduction of 22.7% [32].

Fig. 8 Scarification of tunnel of Via Propora

*F. Stoned pavement in Calusco, Bergamo, Italy*

During March 2003 experiments were conducted to test the efficiency of photoactive binders at reducing NOx through their incorporation in a horizontal structure that occupied an area of 8,000 $m^2$ within an esplanade of Italcementi's new cement plant in Calusco. The structure material was concrete based on TX Aria® cement with precast bilayer paving stones [30]. The concentration of NOx in the area covered by photocatalytic blocks was considerably lower, with a 45% reduction relative to the reference area [16].

*G. Street Borgo Palazzo, Bergamo. Italy*

This project had an active photocatalytic area of about 7000 $m^2$, in which red cobblestones were implanted on the sidewalks and grey cobblestones were used on the road. The approximate length for assessment of the efficiency of these products, treated with TX Aria®, is 500 meters. The IMD in this street is approximately 400 automobiles per hour, while monitoring activities carried out in November 2006 and January 2007 showed a decrease in the concentration of $NO_x$ between 30 and 40%, which is equivalent to modifying the IMD to 250 automobiles per hour [32]. The manufacturer from which these paving stones were bought emphasizes that in order for these products to be completely effective and to recover their initial colors they need to be washed periodically, as the presence of dust or dirt may slightly decrease their effectiveness.

*H. Tunnel Umberto I, Roma*

The tunnel Umberto I of Rome was built in the early twentieth century and is located in the center of the city connecting the street Tritone with the avenue Nazionale, underneath the Quirale Palace. The dimensions of the tunnel are as follows: 348 meters long, 17 meters wide, and 9 meters high. During the month of August 2007 its lighting and ventilation were rehabilitated, and 9000 $m^2$ of ceiling were treated with TX Aria® cement-based paint.

Prior to such remodeling, the tunnel had been subjected to two monitoring evaluations of their pollution level. They measured the environmental conditions, such as temperature, humidity, and rainfall, as well as nitrogen oxide concentration, which were used to study traffic flow and average density. Given the control values, the photocatalytic treatment onto the upper part of the tunnel was shown to cause a 19% decrease in $NO_x$ concentration and a 25% decrease in NO concentration.

The determination of nitrogen oxide concentrations was conducted by ARPA Lazio, the Agency of Environmental Protection of Rome. According to ARPA Lazio, further monitoring activities led to the conclusion that the actual decontaminating efficiency of this infrastructure is greater than the above. Taking into account the tunnel characteristics and lighting system and the weather conditions, this photocatalytic treatment could be used to reduce pollution outdoors, with an actual efficiency between 51 and 60% [32].

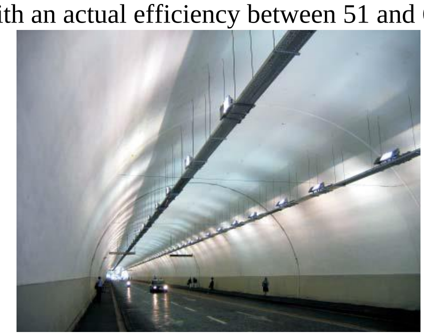

Fig. 9 Tunnel Umberto I, Rome [32]

*I. Castorweg Street in Hengelo, The Netherlands*

The paving Project in Castorweg Street consisted of blocks of photocatalytic concrete with a 5 mm wide upper layer (i.e., active layer) treated with $TiO_2$ which was produced by Struk Verwo Infra. The project had the financial support of the Province of Overijssel (The Netherlands) and was carried out from 2008 to July 2011 jointly by the University of Twente, the University of Eindhoven, the University of Technology in Hangelo, and the company Struyk Verwo Infra.

Approximately a street area of 7500 $m^2$ was treated with decontaminating blocks. In order to test their efficiency, both Castorweg Street and an adjacent street with the same level of pollution were monitored [26]. The efficiency was assessed with laboratory tests that followed the standard ISO 22197-1:2007.

The first measurement did not show a large reduction of $NO_x$ concentration because the suspension of $TiO_2$ that had been used to treat the blocks in May 2010 had been lost after a three month outdoor exposure, even leading to a decrease in photocatalytic efficiency. In December 2010 another $TiO_2$ coating was placed. No significant photocatalytic activity was observed after a month and a half had passed, and after 11 months monitoring results indicated the photocatalytic efficiency was lower than at starting point [29].

## V. Future Applications in Spain

*A. Project Ecofomat*

"Industrial development and application of nanotechnological coatings for removal of contaminants on the surface of construction materials"

The objective of this project is the application of novel coatings based nanoparticles with photocatalytic effect, thereby reducing atmospheric pollution. In particular, it aims to decrease carbon monoxide concentration by up to 75%, volatile organic compounds concentration by up to 80% and nitrogen oxides by up to 90%. Coatings will be applied in a simple and economic way onto construction materials.

The duration of project ECOFOMAT is 3 years. It was initiated in 2010 with an exhaustive bibliographical study and it is now working on the development and formulation of the most adequate photocatalytic systems for real scale application, including the type and composition of nanoparticles, their concentration, stabilizing agents and additives, among other factors.

### B. Project LIFE MINOx-STREET

"Monitoring and modelling NOx removal efficiency of photocatalytic materials: a strategy for urban air quality management"

Project LIFE MINOx-STREET has a total budget of 1,928,619 €, of which 916,913 € are supplied by the European Union [30]. The esteemed duration of the project is 4 years, from 2013 to 2017. It is being developed by collaborating partner INECO (Ingeniería y Economía del Transporte, S.A.), CIEMAT (Department of Environment, Energy, and Technology of Spain) as majority partner, CEDEX (Center of Studies and Experimentation of Civil Constructions), and the City Hall of Madrid [31].

The aim of the Project is to achieve levels of atmospheric pollution that do not pose a health hazard to the public. The specific objectives of the Project are the following:

- To demonstrate and compare the potential applicability of a series of commercial photocatalytic materials, studying how they react with $NO_2$ and $NO_x$, in order to select the most promising solutions for application in urban surfaces under real conditions;
- To provide data from rigorous tests on the physicochemical properties and expected efficiency of several commercial photocatalytic materials, both under controlled and real conditions;
- To obtain the parametrization and settling rate of $NO_x$ on selected photocatalytic surfaces;
- To use photocatalytic materials in real urban settings and to demonstrate their ability to purify air;
- To assess the potential impact of the subproducts generated by the use of photocatalytic products, viz., leached nitrates and suspended particulate matter coming from photoactive TiO2 catalysts, and volatile organic compounds;
- To assess the impact of air purification by the use of combined photocatalytic materials combined in different urban settings at district level, using the prototype;
- To estimate the cost and benefits of this application and other strategies of NOx reduction in urban air.
- Expected results: The results of this project will be the basis of a guide for local authorities on the feasibility and protocols for use of decontaminating photocatalytic materials, properties in urban environments.
- Evaluation of reduction strategies. This technology has the potential to reduce NOx concentration in cities by up to 40% [38].

### C. Project LIFE MINOx-STREET

Project LIFE- EQUINOx will be carried out in Madrid with the aim of demonstrating the efficiency of the asphalt paving application in removing nitrogen oxides contained in urban environments by the addition of titanium dioxide and solar radiation and in reducing the total level of air pollution by up to 25%.

The development of this Project includes not only the demonstration of the efficiency described above, but also includes the methodology for synthesis of photocatalyst material $TiO_2$. In a way this project aspires to develop the concept of "new decontaminating roads", which will contribute, along with other corrective and preventive measures, to improve urban quality air by the reduction of $NO_x$, as established by Directive 2008750/EC.

Project LIFE-EQUINOx will be executed with the collaboration of the City Hall of Madrid, the firms Elsan, based in Madrid, Servià Cantó, in Gerona, and Repsol, in Madrid, and will be coordinated by CARTIF [32].

## VI. Conclusions

The practical application of $TiO_2$ as a decontaminating material calls for further research as its complete efficiency requires optimal conditions of humidity, temperature, light irradiation and cleanliness. Moreover, real scale application cases reveal the importance of the proximity to the emission source and to solar rays.

Furthermore, in order to make test measures under real conditions, it is necessary for the tested location to meet canyon street conditions, so that true decontaminating efficiency values can be measured.

The porosity of the surface on which $TiO_2$ is applied is an additional key factor that influences efficiency, as the surfaces must be kept clean. In locations where pollution levels are high, rainwater may not ensure cleanliness, therefore requiring applications on vertical walls.

Finally, research into the study of photocatalytic products applied on reinforced concrete needs to be conducted since the effect of the catalyst on the reinforcement is not completely known yet.

Once it is checked that $TiO_2$ addition does not negatively affect concrete inherent properties, a study must be conducted to find how to force the disposition of the photocatalytic materials so that it is maximally exposed to solar radiation. Different mechanisms could include pumping, tiers, or taking advantage the shift that occurs by trimix. This will lead to an optimization of cost, as there is no point in distributing photocatalytic material throughout all the cement matrix when only part of it will be exposed to solar radiation.

Coming notices are expected to provide concluding

http://dx.doi.org/10.15242/IIE.E0514557 

information on the technical and economic feasibility of their application on precast materials, such as coating plates for buildings and retaining walls (reinforced or with plates).

Traffic restrictions in cities like Paris in March 2014 due to pollution should encourage reflection and, in spite of the world crisis, make possible the use of the created prototypes in the near future in order to preserve the planet.

## ACKNOWLEDGMENT

The authors would like to thank Lucía Redondo Azurmendi, researcher of the Technical University of Madrid, for her work and contribution to this paper.

## REFERENCES


[1] Ballester, F. (2005). Contaminación atmosférica, cambio climático y salud. *RevEsp Salud Pública*, *79*(2), 159-175.

[2] Díez, F. B. (2003). La evaluación del impacto en salud de la contaminación atmosférica. *Revista de Salud Ambiental*, *3*(2), 102-107.

[3] Ministerio de Agricultura, Alimentación y Medio Ambiente de España. Secretaría de Estado de Medio Ambiente. D.G. de Calidad y Evaluación Ambiental. S.G. de Calidad del Aire y Medio Ambiente Industrial. Inventario de Emisiones a la Atmósfera de España. Available from: http://www.magrama.gob.es/es/calidad-y-evaluacion-ambiental/temas/sistema-espanol-de-inventario-sei-/Sumario_Inventario_de_Emisiones_de_Espa%C3%B1a_OTROS_GASES_-_serie_1990-2011_tcm7-1740.pdf

[4] Instituto Nacional de Ecología. Available from: http://www2.inecc.gob.mx/publicaciones/libros/396/tipos.html

[5] Ministerio de Agricultura, Alimentación y Medio Ambiente de España. Available from: http://www.prtr-es.es/NOx-oxidos-de-nitrogeno,15595,11,2007.html

[6] Aránguez, E., Ordóñez, J. M., Serrano, J., Aragonés, N., Fernández-Patier, R., Gandarillas, A., & Galán, I. (1999). Contaminantes atmosféricos y su vigilancia. *Revista española de salud pública*, *73*(2), 123-132.

[7] Spiegelberg, P. S., Téllez, R. A., Rodríguez, M. J. P., Rodríguez, M. T. R., Marín, M. Á. C., Villar, C. B., ...& Mata, R. R. (2012). Ministerio De Agricultura, Alimentación Y Medio Ambiente

[8] Pimpinelli, N., T. De Marco, and D. Locatelli, *Nanotechnology in Cementitious Field.* CTG Italcementi Group.

[9] Fujishima, A., X. Zhang, and D. Tryk, *Heterogeneous photocatalysis: From water photolysis to applications in enviromental cleanup.* International Journal of Hydrogen Energy, 2007. **32**: p. 2664-2672. http://dx.doi.org/10.1016/j.ijhydene.2006.09.009

[10] Ballari, M. M., Yu, Q. L., &Brouwers, H. J. H. (2011). Experimental study of the NO and NO< sub> 2</sub> degradation by photocatalytically active concrete. *CatalysisToday*, *161*(1), 175-180. http://dx.doi.org/10.1016/j.cattod.2010.09.028

[11] Asociación Ibérica de Fotocatálisis. Available from: http://www.fotocatalisis.org/

[12] Páez, C. A. J., & Ocampo, G. T. (2006). La fotocatálisis: aspectos fundamentales para una buena remoción de contaminantes. *Revista Universidad de Caldas*, 71-88

[13] Balauru, I.P. and K. Chong, *Nanotechnology And Concrete: Research Opportunities.* Proceedings of ACI Session on Nanotechnology of Concrete: Recent Developments and Future Perspectives, 2006: p. 15-28.

[14] CLEAM -Construcción Limpia, Eficiente y Amigable con el Medioambiente Tarea 6.2 "Separación selectiva de residuos". /Tarea6.3"Caracterización de propiedades descontaminantes de morteros con nano-$TiO_2$".(Programa CENIT). Available from: www.cleam.es

[15] De Lasa, H. I., Serrano, B., &Salaices, M. (2005). *Photocatalytic reaction engineering* (p. 193). New York: Springer. http://dx.doi.org/10.1007/0-387-27591-6

[16] Maury, A., & De Belie, N. (2010). Estado del arte de los materiales a base de cemento que contienen $TiO_2$: propiedades auto-limpiantes. *Materiales de Construcción*, *60*(298), 33-50. http://dx.doi.org/10.3989/mc.2010.48408

[17] Bordes, M.C., et al., *Determinación de la función fotocatalítica de recubrimientos sobre soporte cerámico.* Boletín de la sociedad española de cerámica y vidrio, 2007. **46**: p. 273-279. http://dx.doi.org/10.3989/cyv.2007.v46.i6.212

[18] Guerrini, G. L., & Peccati, E. (2007, October). Photocatalyticcementitious roads for depollution. In *International RILEM symposium on photocatalysis, environment and construction materials* (pp. 8-9).

[19] Herrmann, J. M. (1999). Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catalysis Today, 53(1), 115-129. http://dx.doi.org/10.1016/S0920-5861(99)00107-8

[20] Fujishima, A., & Zhang, X. T. (2006). Titanium dioxide photocatalysis: present situation and future approaches. ComptesRendusChimie, 9(5-6), 750-760. doi: DOI 10.1016/j.crci.2005.02.055 http://dx.doi.org/10.1016/j.crci.2005.02.055

[21] Hüsken, G., Hunger, M., & Brouwers, H. J. H. (2009). Experimental study of photocatalytic concrete products for air purification. Building and Environment, 44(12), 2463-2474. doi: DOI10.1016/j.buildenv.2009.04.010 http://dx.doi.org/10.1016/j.buildenv.2009.04.010

[22] Roy, S., M.S. Hegde, and G. Madras, *Catalysis for NOx abatement.* AppliedEnergy, 2009. **86**: p. 2283-2297. http://dx.doi.org/10.1016/j.apenergy.2009.03.022

[23] Cárdenas Ramírez, C. (2012). *Evaluación de las propiedades físicas y fotocatalíticas de cemento adicionado con nanopartículas de dióxido de titanio* (Doctoral dissertation, Universidad Nacional de Colombia, Sede Medellín).

[24] Lacombe, S., & Keller, N. (2012). Photocatalysis: fundamentals and applications in JEP 2011. *Environmental Science and Pollution Research*, 1-4.

[25] Rousseau, P., Drouadaine, I., &Mazé, M. (2009, May-June). Le procédéNOxer® : du développementauxmesures de dépollution sur site. *Revue générale des routes et de l'aménagement*.

[26] Ballari, M. M., &Brouwers, H. J. H. (2013). Full scale demonstration of air-purifying pavement. [Article]. *Journal of Hazardous Materials, 254*, 406-414. doi: 10.1016/j.jhazmat.2013.02.012 http://dx.doi.org/10.1016/j.jhazmat.2013.02.012

[27] Crispino, M., &Vismara, S. (2010). Innovative Photocatalytic Pavements Presentation at InternationalSustainable Pavements Workshop. Airie, VA.

[28] Beeldens, A. (2008). Air purification by pavement blocks: final results of the research at the BRRC. Ljubljana, Slovenia.

[29] FYM. Italcementi Group, Spain. Available from: http://www.fym.es

[30] CISDEM-CSIC-UPM

[31] Italcementi Group. Available from: http://www.italcementigroup.com

[32] Jean, R. (2013). 8. Field Evaluation of Photocatalytic Pavements. *Photocatalytic degradation of NOx by concrete pavement containing* $TiO_2$, 30.

[33] Overman H.T.J., Simulation model for NOx distributions in a street canyon with air purifying pavement, Master Thesis, Department of Construction Managemen& Engineering, Faculty of Engineering Technology, University of Twente, Enschede, the Netherlands, 2009.

[34] LUREDERRA: Centro Tecnológico. Available from: http://www.lurederra.es/noticias_detalle.php?id=27

[35] Universidad Pública de Navarra, España. Available from: http://www.unavarra.es/actualidad/noticias?contentId=152466

[36] Available from: http://ec.europa.eu/environment/life/project/Projects

[37] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas. Disponible en: http://www.ciemat.es

[38] CARTIF: Centro Tecnológico. Available from: www.cartif.com