Development of standardized method for the determination of the degradation of nitric oxide (NO) in the air by photocatalytic materials: Inter-laboratory validation tests

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Abstract: The need of a uniform experimental procedure for assessing the performance of photocatalytic inorganic materials contained in building materials led the European Committee for Standardization (CEN/TC386/WG2) to elaborate a Technical Specification (TS).Taking into consideration the importance of the effects which will be of possible variations in the implementation of the reference method, parallel photocatalytic tests according to the TS were performed in the current study.

6 European labs were participated in an inter-laboratory exercise where the experiments had to be done in a special design CEN reactor using LED system. The experimental procedure and conditions were taken from the draft TS and were referred to the average irradiance, inlet NO & NO_2 concentration, T^oC and RH inside the reactor, flow and reactor net volume. Identical photocatalytic samples were provided to all participants. The results obtained from the 6 labs showed a variation between 18% and 31% on the photocatalytic NO conversion while the mean value was 26%. The corresponding photocatalytic rate was ranged between 2600 μg/m^{2}h and 4100 μg/m^{2}h presenting a mean value of 3400 μg/m^{2}h. The homogeneity of the lamp and the homogeneity of the deposition of TiO_2 are the main factors impacting the results.

Keywords: NO photocatalysis, building materials CEN Technical Specification, inter-laboratory tests

1. Introduction

Heterogeneous photocatalysis is an efficient and clean technology for the degradation of air pollutants. It represents an emerging environmental control option for the efficient removal of chemical pollutants in air. This process involves a semiconductor catalyst, regularly titanium dioxide (TiO2), which is activated with ultraviolet light of the appropriate wavelength.

Over the last years, heterogeneous photocatalysis has received great attention and has become a very promising technology for the remediation of environmental pollution owing to the fact that it can lead to the complete destruction of a great number of organic and inorganic compounds with low energy costs. In addition, particular interest has been given to the titanium dioxide (TiO_2) photocatalysis, which is found to exhibit unique advantages in efficiently decomposing low concentrations of inorganics and VOCs under mild conditions in comparison to other available remediation technologies, such as the thermal and catalytic incineration technologies (Maggos T.), Fu, Jacobi, Blanco). For example, while one NOx control methodology is to reduce NOx back to N_2 (Zhang), another approach is to oxidize NO to NO_2 and HNO_3 along the general direction of nitrogen fixation. Overall, the NOx photocatalytic oxidation offers the following distinctive advantages: (1) no extra reactants are required and (2) NOx is recycled or recovered as nitric acid, which constitutes a potential raw material for fertilizers.

The use of the TiO_2 photocatalyst in cementitious and other construction materials has become an interesting approach over the last decades for the removal of air pollutants in urban areas (Fujishima). Concrete pavement surfaces and external building surfaces constitute optimal media for the application of photocatalytic materials than can reduce air pollution in indoor and outdoor environments. A number of laboratory studies (Strini; Poon and Cheung,; Demeestere) as well as several pilot projects can nowadays affirm the depollution effectiveness

of such photocatalytic building materials. Furthermore, it is proven that even in real complex site conditions, the photocatalytic air purification effect of the (photocatalytic) construction materials (cementitious layer) remains effective (Guerrini and Peccati; Beeldens).

In addition to the materials' construction quest, in the literature of photocatalysis, special care has also been given to the optimal reactor configuration. Several different laboratory reactor designs are nowadays reported in the literature, including fixed bed annular reactor configurations, batch reactor, semi-batch reactor with quartz flat window, circulating fluidized bed (CFB) reactor, microchannel reactor, honey comp monolith reactor, TiO2-coated fibre-optic cable reactor, annular venture reactor etc. (Tomasic). In the majority of studies, a continuous-flow air pollutant stream is employed (dynamic systems), and the photo-efficiency of the materials is evaluated by the difference in the air pollutant concentrations, which are recorded at the steady states before and after the system's irradiation. However, further investigation on the matter is needed since the relationship between the employed photocatalytic reactor configuration, the adopted operational conditions and the photocatalysts' nature still remains quite unexplored.

It is the purpose of this study to evaluate through an inter-laboratory comparison the TS (technical specification) prepared by the European Standardisation Committee for assessing the performance of photocatalytic inorganic materials contained in cement mortars and limes, ceramic-based matrices, paints and materials deposited as thin films or coatings on a variety of substrates. The photocatalytic abatement rate was calculated from the observed rate by eliminating the effects of mass transfer.

2. Scope and Method

Labs from 6 European countries (Torino University/Italy, Fraunhofer Institut/Germany, Belgian Road Research Center (BRRC)/Belgium, Cristal Corporate/U.K, TERA Group and IPREM (Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux (PAU)/France, NCSR "Demokritos"/ Greece) were participated in an inter-laboratory validation exercise where the experiments had to be done in a special design CEN reactor using LED system. The experimental procedure and conditions are described hereafter.

The principle of the current method consists in measuring the photocatalytic abatement of nitric oxide (NO) by photocatalytic building materials using a Continuous Stirred-Tank Reactor (CSTR) with flow tangential to the specimen testing materials were provided by CRISTAL Company (CC) and Torino University (TU). The residual NO and NOx concentration at the CSTR outlet was measured by a chemiluminescence analyzer (EN ISO 7996).

2.1. Apparatus

Table 1. Experimental conditions

Parameter	Symbol	Measurement unit	Nomimal value	Variation allowed
Average irradiance	I	W m^{-2}	10	5%
Inlet NO_2 concentration	$C_{NO_2}^{IN}$	ppmv	<0.025	-
Inlet NO concentration	C_{NO}^{IN}	ppmv	0.50	10%
Temperature inside the reactor	T	^{o}C	25	±5^{o}C
Gas relative humidity at 20^{o}C inside the reactor	RH	%	40%	±5%
Flow	F	dm^3 min^{-1}	1.6	10%
Reactor net volume	V_r	dm^3	3.2	20%

The photocatalytic activity test was carried out using chromatographic grade air to which NO was added in such an amount as to simulate a high degree of air pollution. The NO concentration was set to (0.50 $\pm$ 0.05) ppmv. The mass flow controllers, calibrated and traceable, ensure a maximum flow consistent with that needed for a correct test execution. The gas mixture preparation system ensure a relative humidity of (40 $\pm$ 5) % inside the CSTR reactor. The relative humidity was measured inside the reactor *R* by means of a hygro-thermometer (Table 1)

Irradiation was provided by Omicron FSLED device, being located horizontally, at a distance of approximately ~45mm from the photocatalytic material. The total UV light intensity measured on the samples' surface was on average 10 Wm^{-2}.

The reaction chamber was built with NO inert materials (polymethylmethacrylate) and is gas-tight. On top, the chamber has a flat window that is transparent to the light emitted by the illumination system and vertically incident to the specimen. This flat window, transparent to the wavelengths used is made up of borosilicate glass and it is 4 mm thick to ensure sufficient strength and also removable to allow for specimen positioning. The fan inside the reactor ensures perfect mixing inside the reaction chamber. The fan is placed on a support having a hole with diameter equal to the fan opening and axial to the fan axis. The support has lateral holes that ensure full air mixing inside the chamber. The fan provides nominal flows at the nominal supply voltage of 70 $m^3\ h^{-1}$. The fan flow shall be varied by varying the supply voltage by an appropriate power supply of continuous variable output voltage

The NO_x concentration is measured with a chemiluminescence NOx analyzer (Environment S.A AC42M), which was connected in line to the outlet of the reactor.

2.2. Calculation of Photocatalytic Performance

The following values are measured in sequential order in order to calculate the conversion in the absence of the specimen.

C^{IN}: concentration of NO and NO_2 at reactor inlet;

$C^{OUT,DARK}$: concentration of NO and NO_2 at reactor outlet under stable conditions in the dark (no illumination);

$C^{OUT,light}$: concentration of NO and NO_2 at reactor outlet under stable conditions with irradiation (lamp on).

The test result is expressed as conversion $\eta_{NO,lamp}^{PHOTO}$ calculated as follows:

$$\eta_{NO,lamp}^{PHOTO} = \frac{C_{NO}^{OUT,DARK} - C_{NO}^{OUT,LIGHT}}{C_{NO}^{OUT,DARK}} \quad (1)$$

The conversion values in the absence of specimen are acceptable if $\eta_{NO,lamp}^{PHOTO}$ <0.02 (2 %).

Then the Conversion in the dark and in the presence of specimen is calculated.

The value $C_{NO,S}^{OUT,DARK}$ in the presence of specimen correspond to the NO concentrations at the outlet of the reactor containing the specimen in the dark.

The test result is expressed as conversions η_{NO}^{dark} and calculated as follow:

$$\eta_{NO}^{dark} = \frac{C_{NO}^{IN} - C_{NO,S}^{OUT,DARK}}{C_{NO}^{IN}} \quad (2)$$

Then the conversion under irradiation in the presence of specimen is measured**.** The concentration is measured by conveying the test gas into the reaction chamber with the lamp on. The NO and NO_2 concentrations at reactor outlet shall be monitored continuously. In this case $C_{NO,0}^{OUT,LIGHT}, C_{NO_2,0}^{OUT,LIGHT}$ are measured at fan speed vnom. In order to determine the mass transfer effect on the total NO photocatalytic degradation rate, measurements at different fan speeds are carried out. After decreasing the potential at step i, the NO and NO_2 concentrations at reactor outlet are measured continuously.

The test result is expressed as conversions $\eta_{NO,i}^{total}$ and $\eta_{NO_2,i}^{total}$ calculated from the following equations:

$$\eta_{NO,i}^{total} = \frac{C_{NO}^{IN} - C_{NO,i}^{OUT,light}}{C_{NO}^{IN}} \quad (3)$$

$$\eta_{NO_2,i}^{total} = \frac{C_{NO_2,i}^{OUT,light} - C_{NO_2}^{IN}}{C_{NO}^{IN}}$$

Furthermore the photocatalytic rates are calculated as the difference between the abatement rates and the rates observed in the dark.

$$r_{NO,i}^{photo} = \frac{613\,F}{S}\left(\frac{\eta_{NO,i}^{total}}{(1-\eta_{NO,i}^{total})} - \frac{\eta_{NO}^{dark}}{(1-\eta_{NO}^{dark})}\right) \quad (4)$$

3. Results and Discussion

The results of the % NO photocatalytic conversion and photocatalytic rate from the 2 samples used in the inter-laboratory test (CC and TU) are presented in figure 1. The results obtained for CC samples showed a variation between 15% and 35% on the photocatalytic NO conversion while the mean value was 25%. The corresponding values for TU samples were 19% up to 31% with a mean value 25%, while the corresponding photocatalytic rate was ranged

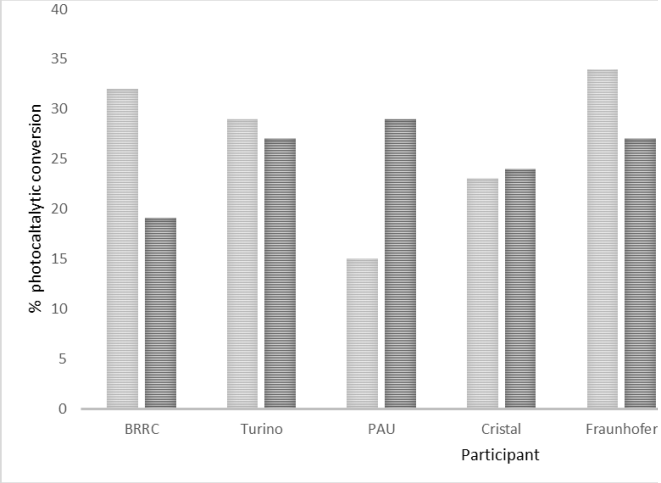

Figure 1. % NO photocatalytic conversion of two types of samples during an inter – laboratory test

between 2600 μg/m^{2}h and 4100 μg/m^{2}h presenting a mean value of 3400 μg/m^{2}h Although deviations between the results are noticed, the differences are much lower than other inter-laboratory tests where different apparatus were used by the participated labs. The main conclusion of the current test is that the homogeneity of the lamp and the homogeneity of the deposition of TiO_2 are the main factors impacting the results.

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