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Durability of Cementitious Photocatalytic Building Materials

Elia Boonen[a,*], Anne Beeldens[a], Inge Dirkx[b,*], Veerle Bams[b]

[a] Belgian Road Research Centre (BRRC), Woluwedal 42 – 1200 Brussels, Belgium
[b] Belgian Building Research Institute (BBRI), Avenue P. Holoffe 21 – 1342 Limelette, Belgium

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ABSTRACT

Photocatalytic building materials have been shown to be a promising remediation technique for air pollutants such as NO_x and VOC's. However, there are still doubts and questions about the durability of the air cleaning characteristic in time. In this respect, a pre-normative research is being undertaken at BRRC as a first step towards evaluation of the life time of these photo-active air purifying products. This is done by combining and adapting existing durability tests for cement-based materials with standardized test methods to determine the photocatalytic activity. First results of this research are presented here, including a state-of-the-art on accelerated ageing testing as well as the validation of applicable ageing procedures in combination with a normalized evaluation test for photocatalytic NO_x abatement. Finally, recommendations for future work regarding durability testing on photocatalytic building materials are also given.

1. Introduction

Starting from the pioneering work on photobleaching of dyes in the early 20th century [1,2] and the Japanese research later on [3–5], the interest in photocatalysis grew considerably over the last 3 to 4 decades. Since then, photocatalytic building materials with incorporation of titanium dioxide, have been shown to be a promising technique to reduce a number of air contaminants such as NO_x and VOC's, especially at sites with a high level of pollution: highly trafficked canyon streets, road tunnels, urban environment, etc. [6]. In addition, the combination of TiO_2 with cement-based products offers some synergetic advantages, as the reaction products can be adsorbed at the surface and subsequently be washed away by the rain [7].

However, more recent applications have demonstrated that the durability of the air cleaning characteristic with time remains challenging, especially for the application in pavement and building materials [8–10]. Hence, there are still questions and doubts about the "life time" of these photoactive air-purifying products. In this respect, a two-year pre-normative research project is currently being undertaken at BRRC, in partnership with BBRI, as a first step towards determining and evaluating the durability of the photocatalytic activity in time.

The major objective of this research study is thus to develop standardized test procedures to be able to determine the durability of the photocatalytic efficiency in time by combining existing durability (accelerated ageing) tests with methods to determine the photocatalytic activity. In addition, the focus is on *cement-based* air purifying building materials. This is also connected to the normalization work being carried out for the moment within CEN Technical Committee 386 "Photocatalysis" [11].

In the present paper, first results are presented including a state-of-the-art report on accelerated ageing testing for cement-based materials and validation of selected ageing procedures combined with and adapted to normalized photocatalytic activity testing regarding NO_x abatement. In addition, results are discussed in view of recommendations for future work on evaluation of the durability of photocatalytic cement-based building materials.

2. Materials and methods

In a first phase, a state-of-the-art report (see Appendix A) on accelerated ageing tests applicable to cement-based building materials was set-up. Here, a division has been made in three main areas of ageing tests: abrasion (including the wearing effect from possible traffic passing over the surface), freeze-thaw resistance, and artificial weathering with UV exposure and humidity.

Next, a first selection of applicable ageing procedures was made based on practical feasibility and compatibility with the photocatalytic evaluation test(s):

* Corresponding authors.
E-mail addresses: e.boonen@brrc.be (E. Boonen), Inge.dirkx@bbri.be (I. Dirkx).

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Table 1
Selected, commercial test materials[a].

Material	Type of product	Type of application – Activity	Ageing tests			
			Abrasion (PEI or Böhme)	Freeze-thaw with salt (SLAB-test)	Freeze-thaw without salt	UV and humidity (ISO 4892-3)
1	Paving Block (TiO_2 in bulk)	Horizontal – Air purification	X	X		
2	Active cement with TiO_2	Horizontal (road concrete) – Air purification	X	X		
3	Paving Block (coating)	Horizontal – Air purification + self-cleaning	X	X		X
4	Cementitious skim coat	Vertical – Air purification (+ self-cleaning?)		X	X	X
5	Transparent coating	Horizontal + vertical Air purification + self-cleaning	X	X	X	X
6	Coating	Horizontal + vertical Air purification + self-cleaning	X	X	X	X
7	Exterior paint	Vertical Air purification + self-cleaning			X	X
8A, 8B	Nano-titania coatings	Horizontal + vertical Air purification + self-cleaning	X	X	X	X

[a] For reasons of confidentiality the commercial names of the products have been omitted.

1) Abrasion tests

- Surface abrasion test for glazed ceramic tiles following NBN EN ISO 10545-7:1999 [12] for coatings applied on the surface of the building material, also known as the PEI (Porcelain Enamel Institute) test.
- Böhme abrasion test according to Annex H of NBN EN 1338:2003 (concrete paving blocks) [13], for products where the active TiO_2 is applied in the bulk of the material.

2) Freeze/thaw resistance

- *with* de-icing salt: “Slab test” following NBN EN 1338, Annex D
- *without* de-icing salt: Slab without addition of NaCl to the ponding water

3) Hygrothermal cycles with UV-lighting

In a QUV-chamber with exposition to UV-A lamps (340 nm) in accordance with NBN EN ISO 4892-3:2006 [14], following the guidelines in paragraph 4.1.4 of NBN EN 1871:2000 (road marking paints) [15], consisting of cycles of each:

- 8 h UV-A at 0.68 W/m^2 and 60 ± 2 °C.
- 4 h condensation at 50 ± 2 °C.

In addition, a range of commercially available test materials was also selected based on representativeness in the market, difference in type of product, in initial photocatalytic activity, and in application (horizontal-vertical). These are indicated in Table 1: photocatalytic concrete pavement blocks (2 types), road concrete with active cement (2 types of surface finish), one cementitious skim coat and different photoactive coatings and paints. For the evaluation of all these samples before and after ageing, the air purifying activity according to ISO 22197:2007 [16] for NO_x abatement was determined, as at this time there was no other official European or international standard available. A CEN Technical Specification[1] on the determination of the degradation of nitric oxide is currently under enquiry at European level [11] which would be more suitable for the rough building materials considered here [17]. However, for the test conditions and materials used (see below), it has been verified before [18] that diffusion limitations in our ISO reactor could be neglected.

Fig. 1. Natural ageing on the roof top of the BRRC building in Sterrebeek (Belgium).

Furthermore, photocatalytic activity for NO is expressed in terms of the *photocatalytic deposition velocity k* in [m/h], assuming first-order uptake kinetics and negligible transport limitations from the gas phase to the solid surface [19]:

$$k_{NO} = \ln\left({}^{c_0}/{}_{c_t}\right) \cdot F/A \quad (1)$$

where c_0 and c_t are the reactant concentrations at the inlet and exit of the photoreactor, respectively. In fact, this parameter refers to a first-order reaction rate coefficient independent of the applied flow rate F [cm^3 s^{-1}] and the active surface (A) [cm^2]-to-volume ratio of the reactor used, also in line with the theoretical formulation of [17] when mass transfer limitations can be neglected. Following conditions were applied in this research:

- NO_{in} = 1 ppmV;
- relative humidity (RH) = 50%;
- flow rate F = 3 l/min;
- surface area A = 20 × 10 cm^2;
- UV-A irradiance I = 10 W/m^2.

Finally, part of the samples was also placed outside on 17/6/2015 and on 8/9/2015 at the roof of the BRRC building in Sterrebeek, Belgium (Fig. 1) to be able to study the natural ageing of the materials.

[1] FprCEN/TS 16980-1 “Photocatalysis – Continuous flow test methods – Part 1: Determination of the degradation of nitric oxide (NO) in the air by photocatalytic materials”, April 2016.