Cement and Concrete Research 71 (2015) 124–131

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Characteristics and efficiency of photocatalytic cementitious materials: Type of binder, roughness and microstructure

E. Jimenez-Relinque, J.R. Rodriguez-Garcia, A. Castillo, M. Castellote *

Institute of Construction Sciences Eduardo Torroja, IETcc-CSIC, Serrano Galvache, 4, Madrid, Spain

ARTICLE INFO

Article history:
Received 25 September 2014
Accepted 6 February 2015
Available online 13 March 2015

Keywords:
Photocatalysis (C)
Type of cement (D)
NOx oxidation and self-cleaning (C)
Roughness (B)
Microstructure (B)

ABSTRACT

This work aims to study the effect of addition of photocatalyst on the characteristics of TiO_2 modified mortars and the influence of type of binder, surface roughness and microstructure, on their photoactivity for self-cleaning of organic dyes (rhodamine B and methylene blue) and NOx degradation. Mortars with four different types of cements and three levels of roughness were prepared. From the results, it was found that the available active surface is a parameter more influential than surface roughness for assessing photocatalytic efficiency. Concerning the composition of the mixes, the classification according to photocatalytic efficiency was the same for both NOx and self-cleaning, being, in decreasing order: Portland cement (quite similar to calcium aluminate cement for NOx), fly ash and slag mortars. The difference has been explained on the basis of oxidation-reduction potentials and photoabsorption energy of the different constituents of cementitious matrix.

1. Introduction

Air quality continues to be a very important issue for public health, the economy and the environment. As an example in 2010, ceilings for NOx were exceeded by 11 out of 12 countries, with 7% of European citizens exposed to NO_2 levels above the EU limit values [1]. Furthermore, the number of buildings with large exposed elements is increasing all over the world. These structures must be periodically cleaned usually by manual procedures that involve high maintenance cost and risk.

In this context, the implementation of heterogeneous photocatalysis in construction materials has emerged as a promising technology to tackle these two important issues. Indeed, the incorporation of photocatalyst provides air decontamination [2–5], self-cleaning [6], self-sterilizing [7], and anti-fogging properties to construction materials. Even, more recently, the possibility to eliminate pollen from the air [8] or deposited soot [9] has been postulated. These effects have been achieved by incorporation of nanoparticles, mainly TiO_2, into the materials, in bulk or as surface coatings. Among these materials, there is a growing interest in using cement-based materials (e.g. cement paste or mortar and concrete) as supports due to their strong binding property, porous structure and compatibility of their alkaline pH with TiO_2.

The interactions of TiO_2 nanoparticles with cementitious materials have been recently started to be investigated from different points of view. Hydration [10], carbonation [11], mechanisms of depollution and self-cleaning [3,4,6,12–16], microstructure [17,18], fresh properties and mechanical behavior [11,13,19–22], addition of different types of aggregates, even RCDs [23] are some of the examples studied, finding in some cases contradictory results, mainly regarding influence in porosity and resulting mechanical strength. Concerning roughness of the surface, Hüsken et al. (2009) established that high substrate roughness values were favorable for air purification due to the availability of higher active surface area [24]. Other authors were in agreement with these results [25,26], and recognized the advantage of roughness surface to TiO_2-particle retention. On the other hand, Zhang et al. [27], evaluated the effect of this parameter on self-cleaning activity. In this case, the results show that the specimens with ground surface performed better than the corresponding specimens with casting surface (bottom surface in Petri dishes). However, the difference was not significant [27].

Despite the previous studies carried out about the interaction between TiO_2 and cement materials, the influence of different types of binders and surface roughness has not been fully evaluated. This work aims to study the effect of cement matrix composition, surface roughness and microstructure on the photocatalytic activity of TiO_2 modified mortars for NOx degradation and self-cleaning of organic dyes. Additional study of fresh mortar properties, its mechanical behavior and microstructural changes caused by the introduction of TiO_2 nanoparticles is reported.

2. Materials and methods

2.1. Materials and samples preparation

Normalized mortars (water/cement ratio = 0.5 and cement/sand ratio = 1/3) with four different types of cements: ordinary Portland (OPC), calcium aluminate (CAC), blast furnace slag (SC) and fly ash (FAC) were prepared. Samples including 2% of titanium dioxide

* Corresponding author. Tel.: +34 913020440.
E-mail address: martaca@ietcc.csic.es (M. Castellote).

http://dx.doi.org/10.1016/j.cemconres.2015.02.003
0008-8846/

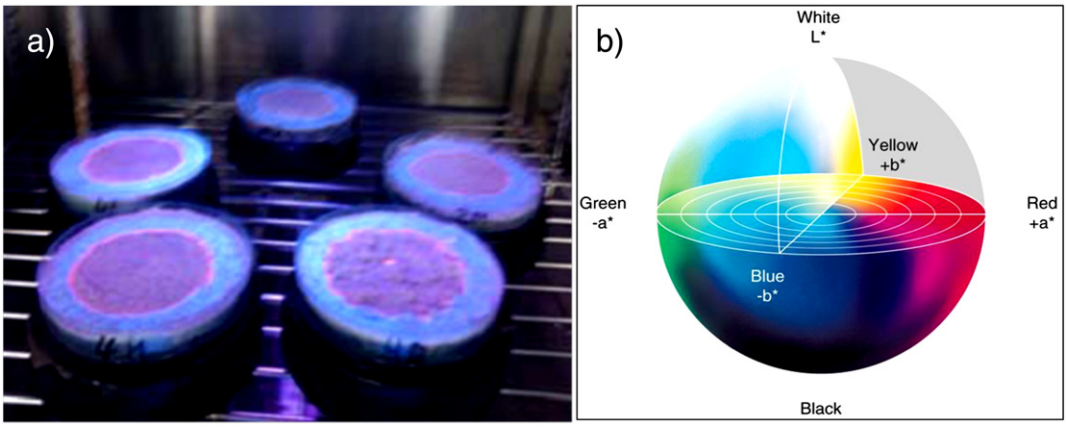

Fig. 1. a) Specimens with RhB dye irradiated by UV light. b) Three-dimensional CIELAB system.

(Aeroxide® TiO_2 P25-PhC) on weight of cement and samples without TiO_2 were also made. Mortars with three different surface roughness were prepared according to average deviation from the horizontal plain: below 0.1 mm (fine specimens, F), between 0.5 mm and 1 mm (medium specimens, M) and above 1 mm (rough specimens, R).

The mixing procedure was carried out following the standard UNE-EN-196-1. Mortars were cast in two types of moulds, 40 × 40 × 160 mm blocks and Petri dishes with 90 mm diameter and 10 mm height, and were cured in humid chamber for more than 28 days.

2.2. Characterization of mortars

Mortar consistency and occluded air in fresh state were measured following the procedure described in the Standard EN 1015-3-Part 3 and UNE-EN 1015-7 respectively. Compressive and flexural tensile strengths of mortars were determined according to the UNE-EN 1015-11 standard. The two residual portions of the prisms after the flexural strength test were used for the compressive strength test. All tests were carried out on duplicate specimens.

Samples were characterized through mercury intrusion porosimetry, X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to evaluate their elemental mineralogical composition and microstructure. The optical absorbance of mortar samples was measured by UV–visible diffuse-reflectance spectroscopy (UV–vis DRS).

2.3. Photocatalytic efficiency

2.3.1. NOx degradation

Efficiency of photocatalytic mortars to remove NOx was analyzed using a borosilicate glass reactor with a total volume of 2.81 l. A UV lamp emitting UVA radiation at an optimum of 365 nm located outside the reactor was used (Osram Ultravitalux 300 W).

NO gas diluted in normalized air with an initial concentration of 1000 ± 50 ppb was used. The bottle of NO contains a small amount of NO_2 (<7%). Two mass flow controllers were used to prepare the mixture supplying a flow rate of 3 l min^{-1}. When the NO concentration in the reactor reached equilibrium, the lamp was turned on. Relative humidity and temperature were set at 30% and 23 °C for all tests. The sample was illuminated for 1 h and changes in NO and NO_2 concentrations were continuously recorded by a chemiluminiscence NOx analyzer (model AC32M Environmental S.A.). The amount of NOx (NO + NO_2) removal was calculated through Eq. (1).

$$NOx_{removed} = [(NO_x - NO_{xo})/NO_{xo}] \cdot 100 \quad (1)$$

where NO_x is the final pollutant concentration after the irradiation test. NO_{xo} is the initial NOx concentration.

2.3.2. Self-cleaning performance

Self-cleaning capability of photocatalytic mortars was determined by monitoring the discoloration of organic dyes (Rhodamine B (RhB)-UNI 11259:2008 and methylene blue (MB)-ISO 10678:2010), even though dye-sensitization has been reported [12]). Experiments were carried out for both dyes according to the procedure given in the standard UNI-11259:2008 with some modifications. While the standard recommends 0.5 ml of RhB solution 0.5 g l^{-1} ± 0,005 g l^{-1}, the current study used 6 ml of solution, either RhB (0.0083 g l^{-1}) or MB (0.015 g l^{-1}). The purpose of change was to obtain a homogeneous distribution over the entire surface of specimens.

Color measurements were taken directly on the surface of each specimen at different times of illumination with a portable spectrophotometer CM-2300d-Konika Minolta. For each chromatic characterization, the mean value of a series of at least 3 measurements was calculated.

The results were expressed according to the CIELAB system (Fig. 1) [4,13]. Reading L^* defines lightness, a^* and b^* denote chromaticities (a^* for red/green and b^* for yellow/blue). The percentage of discoloration was expressed with the coordinate of dominant color of dye a^* or b^* for RhB and MB, according to Eqs. (2a) and (2b), respectively.

$$\%\ \text{of color change} = [(a_0^* - a_t^*)/a_0^*] \cdot 100 \quad (2a)$$

$$\%\ \text{of color change} = [(b_0^* - b_t^*)/b_0^*] \cdot 100 \quad (2b)$$

where a^*_0 and b^*_0 are the color intensity coordinates of specimens before the UV irradiation. a^*_t and b^*_t are the color intensity coordinates of specimens at t hours of irradiation.

Table 1
Summary of results for the different mixes: consistency, fresh apparent density, occluded air, compressive and flexural tensile strengths.

Sample	Flow value (cm)	Occluded air (%)	Compressive strength (MPa)	Flexural strength (MPa)
OPC	17.5	4.4	64.0	8.6
OPC-PhC	15	4.3	61.5	9.2
SC	16	4.3	46.2	11.1
SC-PhC	13.5	4.2	44.2	10.3
FAC	16.5	3.0	50.3	7.7
FAC-PhC	14	3.5	41.9	7.6
CAC	15.5	3.5	45.0	6.1
CAC-PhC	12	3.6	44.2	6.2