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Quantification of hydroxyl radicals on cementitious materials by fluorescence spectrophotometry as a method to assess the photocatalytic activity

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ABSTRACT

The production of hydroxyl radicals ($OH^{\bullet}$) by several photocatalytic cementitious materials was quantified by an adaptation of Terephthalic acid (TA) as probe method for fluorescence spectrometry (TA-FL method) for construction materials. Six different materials were evaluated for $OH^{\bullet}$ using the method developed, and the photocatalytic activity was compared with the NO_x degradation rate, obtaining a positive relationship between both parameters even though the rate of NO_x degradation was significantly larger than that of the $OH^{\bullet}$ detected. The difference could not be attributed exclusively to the contribution of $^{\bullet}O_2-$. Thus, it has been postulated that most of the NO_x degradation takes place through the holes, trapped in the surface of the photocatalyst, in equilibrium with $OH^{\bullet}$ in the bulk solution, which still makes the quantification of $OH^{\bullet}$ as an effective indicator of the photocatalytic performance of cementitious materials.

1. Introduction

Development of photocatalytic construction materials began in the early 1990 [1] with a high potential for very attractive applications such as air pollution remediation [2–4], self-cleaning [3,5], self-disinfection [6–8] and even, very recently, the possibility to eliminate pollen from the air has been postulated [9]. The high versatility of photocatalytic processes has facilitated its application on outdoor construction materials, indoor furnishing materials and road construction materials.

In spite of successful application of TiO_2 photocatalysis in cement based materials, an ideal method to determinate the photocatalytic activity is still not available. In general, their depolluting properties are evaluated through air purification tests (JIS R1701, ISO 22197, UNI 11247 and 11238); and the self-cleaning activity using organic dyes as pollutant models, in order to evaluate the dye decomposition and the efficiency in recovering the original color (UNI 11259 and JIS R1703). However, the experimental conditions and data treatment differ in many aspects, even leading to non-comparable results [2]. The differences between the test methods are based primarily on: light source, UV intensity, temperature and humidity, flow rate (in the case of air purification tests), characteristics of test samples and contaminant analyzed. With respect to the air-depollution standards, each test requires often expensive analytical equipment, and a technical support for operation and maintenance [10]. In the case of discoloring methods, the big disadvantage is the unequal distribution of dye films [11] and even in some cases, due to the color of the sample, the colorimetric tests are not feasible.

Another standard method to assess an aspect of the performance of photocatalytic materials is based on measuring the water contact under illumination with ultraviolet light (ISO 27448), since superhydrophilicity influences very much the self-cleaning performance of photocatalytic materials. Due to measurement characteristics, this method cannot be used for evaluation of rough surfaces, porous surfaces or highly hydrophobic materials [12]. However, this is the only method designed to get a result regardless of a specific contaminant.

Recently, semi-quantitative techniques have been proposed based on the photooxidation of organic films deposited on surface, such as stearic acid [13] or resazurin with a sacrificial electron donor (e.g. glycerol) [14]. The latter is more rapid than using stearic acid and correlate reasonably well [15].

Other methods with a more quantitative approach are based on the measurement of the rate of hydroxyl radical ($OH^{\bullet}$) generated by the photocatalytic excited surfaces. In general, it has been reported that this reactive oxygen species is an extremely important reactant in photocatalytic reactions, being frequently assigned as the major species responsible for photocatalytic oxidation pathways [16–20]. However, this species presents some characteristics that make its direct detection difficult, such as a very short lifetime and high reactivity. As a result, a variety of indirect methods through the use of spectroscopic probes has been proposed. The main methods used are Electron Spin Resonance (ESR), UV/Vis absorption spectroscopy, luminescence and

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fluorescence [21]. However, many of these methods use expensive analytical equipment and a long analysis time is required. As an alternative method, a photoluminescence simplified technique has been developed to detect easily the $OH^{\bullet}$ formed. In this method, chemical probes such as terephthalic acid or coumarin, effectively capture $OH^{\bullet}$ and produce strongly fluorescent compounds which can be detected by fluorescence spectrometry [22]. The fluorescence intensity of fluorescent compounds is proportional to the amount of $OH^{\bullet}$ generated. For example, Xiang et al. [16] proposed a concept of "OH-index" to quantitatively characterize the production of $OH^{\bullet}$ on various powder semiconductor photocatalysts using coumarin as a probe molecule. This parameter is quite adequate to compare the formation rate of $OH^{\bullet}$ in different photocatalytic systems. However, the trapping efficiency of $OH^{\bullet}$ formed for coumarin was assumed on the level of about 4.7% [23]. Hirakawa et al. [17] studied the effect of H_2O_2 addition on the $OH^{\bullet}$ formation in TiO_2 suspension by means of terephthalic acid as probe. And, Xiao et al. [18] performed the analysis of $OH^{\bullet}$ formation on carbon-doped TiO_2 nanocrystalline under visible light irradiation.

Taking into account the lack of previous studies about the application of fluorescence probe methods on cementitious construction materials, to determine their photocatalytic activity based on the quantification of $OH^{\bullet}$, it seemed rather interesting to search on this possibility. In the present study, the fluorescence probe method using acid terephthalic as probe was adapted and optimized to quantitatively analyze the amount of $OH^{\bullet}$ on various cement-based materials. The photocatalytic activity for each sample was also measured by NO_x degradation ability and then it was compared with the $OH^{\bullet}$ formation rate. Finally, from the quantitative analysis, the contribution of $OH^{\bullet}$ in the photocatalytic efficiency was analyzed.

2. Materials and methods

2.1. Materials

Six different hardened photocatalytic cementitious materials were tested: three home-made mortars and three commercial pavements.

Mortars (labeled as M) were cast according to the standards UNE-EN-196-1 and UNE-EN-197-1 using three different commercial photocatalytic cements. The water cement ratio was 0.5 and the ratio cement:sand (standard siliceous sand) 1:3. After mixing, the mortars were molded in petri dishes of 90 mm in diameter and 16 mm in height. Fresh mortars were cured for 28 days at >95%RH and 23 ± 2 °C inside the dishes. The other three cementitious materials were commercial pavements (labeled as C) that were supplied from the producers.

Commercial terephthalic acid (TA), 2-hydroxylterephtalic (TAOH), sodium hydroxide (NAOH), powdered photocatalyst (Aeroxide® TiO_2 P_{25} from Evonik), dimethyl sulfoxide (DMSO) and ethylene diamine tetraacetic acid (EDTA) were used without further purification. TA and TAOH were neutralized with NAOH (0.02 M, pH 12.4 ± 0.2).

The source of light used had a sharp emission in the UVA region at 365 nm, and at 404 nm and 436 nm in the visible light spectra. Light intensity was adjusted to 10 ± 0.2 W/m^2. Evaporation of the solutions was controlled using transparent heat control filters (KG1 Heat Absorbing Glass, Edmund optics).

Fluorescence spectra of solutions were measured with a fluorescence spectrophotometer (Perkin-Elmer, LS-55).

2.2. Material characterization

Photocatalytic materials were characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF) using a Bruker Advance-D8-XRD and a Tijer S-8-XRF. Adsorption–desorption measurements were conducted on a Micromeritics NOVA2000 apparatus at 77 K using nitrogen as the adsorption gas and the specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Porosity distribution and pore size analysis were performed by mercury intrusion porosimetry (MIP) using a Micromeritics AutoPore IV 9505. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were recorded using a Varian Cary 5000 UV–Vis spectrophotometer and the absorption edge was done according to the analytical model proposed by Kubelka and Munk [24].

2.3. Fluorescence probe method

$OH^{\bullet}$ formation rate during irradiation of samples was measured by fluorescence (FL) spectrometry using TA as a probe. TA readily reacts with $OH^{\bullet}$ to produce a highly fluorescent product, TAOH (excitation, λ_{exc} = 315 nm; emission, λ_{em} = 425 nm), in alkaline systems.

In aerated aqueous solutions, the trapping factor of free $OH^{\bullet}$ by FL method using TA as probe has been determined to be 35% [25,26] without a significant O_2 dependence. Thus, the amount of TAOH measured is proportional to $OH^{\bullet}$ produced, even under changing conditions of O_2 concentration [27].

To quantitatively determine the concentration of TAOH, a calibration curve was generated by plotting FL intensity at 425 nm against concentration of standard TAOH.

2.3.1. Selection of optimal probe concentration

To establish the optimal probe concentration to capture every $OH^{\bullet}$, the product yield was measured as a function of probe concentration: 150 mg of the reference P_{25} TiO_2 was suspended in 100 ml of aqueous solutions containing TA in the range of 0.5 to 3 mM. The suspensions were kept in the dark under magnetic stirring for 5 h, until the adsorption–desorption equilibrium was reached. After that, the suspensions were exposed to irradiation during different times. Product formation yield was determined measuring the FL spectra of the supernatant liquid after recovering the catalyst by centrifugation.

2.3.2. $OH^{\bullet}$ quantification in hardened cementitious samples

In order to assure that the samples were in the same relative humidity conditions, they were preconditioned for 3 days in a controlled environment at T = (23 ± 5)°C and RH = (60 ± 10)%. A test cell (ϕ 67.53 mm × 40 mm) was glued — on the surface of mortars with silicone, as depicted in Fig. 1. To determine the $OH^{\bullet}$ production, 25 ml of TA (2 mM) was added into the test cell, which was irradiated for 40 min under continuous stirring. FL intensity of the solution was measured at 425 nm at different times of irradiation.

2.4. Photocatalytic efficiency

Photocatalytic activity of hardened cementitious samples was analyzed using nitrogen oxides (NO_x = NO + NO_2) as reference pollutants. NO_x removal ability was tested using a continuous flow reactor based on the requirements of ISO standard 22197-1. NO gas was diluted in pure air until reaching an initial concentration of 400 ± 50 ppb. 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

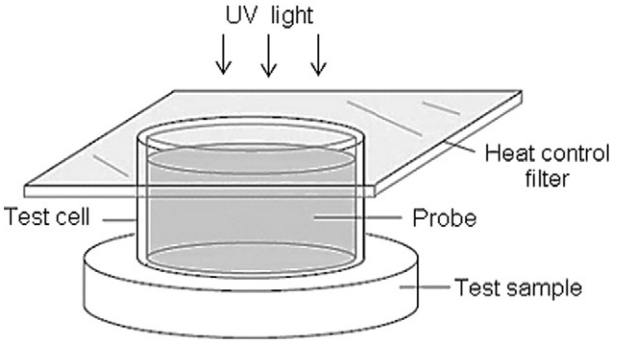

Fig. 1. Schematic setup of $OH^{\bullet}$ quantification method.