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Nota Técnica

METHOD FOR DETERMINING THE PHOTOCATALYTIC POTENTIAL OF PORTLAND CEMENT MORTAR CONTAINING TiO_2 FOR DECOMPOSING THE POLLUTANT NITROGEN MONOXIDE

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Photocatalytic materials can minimize atmospheric pollution by decomposing certain organic and inorganic pollutants using sunlight as an energy source. In this paper, the development of a methodology to measure the photocatalytic potential of mortar containing TiO_2 nanoparticles is reported. The results indicate that up to 40% of NO_x can be degraded by Portland cement mortar containing 30–50% of TiO_2, which validates the method developed for evaluating the photocatalytic potential of materials.

Keywords: photocatalytic potential; titanium dioxide; Portland cement mortar; atmospheric pollutants.

INTRODUCTION

Since discovery of photocatalytic splitting of water by suspensions of titanium dioxide (TiO_2) initially by Fujishima and Honda in 1972 and subsequently studied by Nogueira and Jardim (1998),[1] researchers have been investigating its mechanism and trying to improve its photocatalytic efficiency. TiO_2, a semiconductor (E_{gap} = 3.2 eV), forms three crystalline structures: anatase, rutile, and brokita. Anatase has a higher photocatalytic activity and is used largely due to its high efficiency and low cost. Its principle of operation is based on the generation of electron-hole pair upon absorbing UV light energy. Upon irradiation, electrons in the valence band receive enough power to overcome the energy gap of TiO_2, and thus can be transferred to the conduction band leaving vacancies called holes in the valence band.[1] These electron-hole pairs are strong oxidizing agents and are responsible for the digestion of various organic compounds. Several studies have investigated the possible applications of TiO_2 as a photocatalytic material.[2]

Minimization of the impact of gas pollutants on environment by photocatalysis is a widely pursued goal; several researchers have studied the decomposition of NO_x (Poon and Cheung, 2007; Hüsken *et al*., 2009), NH_3 (Jin *et al*., 2009), and other harmful organic compounds, such as benzene (Du *et al*., 2011), toluene (Demeestere *et al*., 2008), and acetone (Visinescu *et al*, 2005), into innocuous substances.[3]

The use of this technique in civil engineering began in the 1990s in Japan, where companies and universities began to evaluate the photocatalytic abilities of concrete and ceramic tiles.[4]

Thus, in order to implement the technology, a methodology is developed to measure the photocatalytic potential of Portland cement mortar containing TiO_2 nanoparticles in a controlled environment with an UV-A lamp radiation and a known concentration of NO_x gas input.

EXPERIMENTAL

Materials

The cement used in this work was the CP II-32 Z (Portland cement composite with addition of pozzolan), due to its wide use in construction, plain concrete, reinforced concrete, prestressed concrete, precast elements, and other artifacts. Moreover, the material exhibits low permeability, allowing for an ideal application, as recommended by the Brazilian ABNT NBR 11579/91.[5]

Natural washed sand, as fine aggregate, was used for the production of mortar. The water from Curitiba–PR (Brazil) public water supply, considered potable, was used for mixing the concrete strength.

Commercial TiO_2 Evonik Aeroxide P25, predominantly composed of anatase phase, was used as the photocatalytic substance. The primary particle size and surface area of TiO_2 powder was 21 nm and 50 ± 15 $m^2 g^{-1}$, respectively, as specified in the datasheet.

Methodology

Material characterization

Cement and fine aggregate material selected for use in the present study were characterized in accordance with the Brazilian standards (ABNT). Physical, chemical, and mechanical properties of the materials were observed to ensure that there was no interference in the quality of the produced concreted. Table 1 lists the test and methods adopted for evaluating each material.

X-ray diffraction patterns of TiO_2 samples were measured on a Philips X′Pert MPD diffractometer with Cu-Ka radiation operating at 40 kV and 50 mA. The diffraction patterns were used to identify the structural phase of the sample and the Scherrer equation was used to identify the crystallite size:

$$\text{Crystallite size} = k\lambda\left(B\frac{1}{2}\cdot\cos\theta\right)$$

where the value of *k*, the form factor, is 0.90 for a sphere; λ = 1.5406 Å; $B\frac{1}{2}$, base value at half-height (radians); and θ is the diffraction angle.

Scanning electron microscopy (SEM) measurements were carried out on a Philips XL 30 equipped with microprobe analytical X-ray type EDS. The sample TiO_2 powder was previously covered with a thin layer of gold.

Photocatalytic mortar dosages

The photocatalytic study was conducted on samples of simple mortar (thickness = 1.8 cm), covered with a layer of photocatalytic

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Table 1. Methodologies for characterizing cement and aggregates material[5]

Material	Test	Methodology
Cement	Fineness (sieve residue)	NBR 11579/91
	Blaine Fineness	NM 76/98
	Cold Expansion	NBR 11582/91
	Normal Consistency of Cement	NM 43/03
	Specific Gravity	NM 23/01
	Setting Time	NM 65/03
	Compressive Mechanical Strength	NBR 7215/96, NBR 11578/91
	Heat loss	NM 18/04
	Insoluble Residue	NM 15/04
	Mass Content	NM 21/2004
	Calcium Oxide Content	NBR 11-2/09
Aggregate	Fineness Modulus	NBR 7211/09
	Particle Size	NBR 7217/87
	Nominal Maximum Size	NBR 6118/07
	Specific Gravity	NM 53/09
	Unit Weight	NM 45/06
	Water absorption	NM 30/01
	Soil content test	NBR 7218/10

mortar (thickness = 0.2 cm). Simple mortar with cement:sand (2.4 mm):water weight ratio of 1:3:0.4 were prepared. For the photocatalytic mortar layer, the ratio of the components was the same, except that various concentrations of TiO_2 (as cement substitute) were used, according to the data presented in Table 2.

Table 2. Formulation of different TiO_2-containing Portland cement mortar samples

TiO_2 % (in weight of Portland Cement)	Mass of Cement, g	Mass of Sand, g	Mass of TiO_2,g	W/C rate
TiO_2 – 0	--	--	--	--
TiO_2 – 5	50	150	2.5	0.8
TiO_2 - 10	30	90	3	1.0
TiO_2 - 20	30	90	6	1.1
TiO_2 - 50	25	75	12.5	1.4
TiO_2 - 70	20	60	14	1.8
TiO_2 - 90	10	30	9	2.0

The samples were dry cured for ~48 h and wet cured for ~1 week before the tests were conducted for determining the photocatalytic potential.

Photocatalytic test

The photocatalytic potential of Portland cement mortar samples containing varying amounts of TiO_2 was measured using an in-house built PVC cell (100 mm diameter) equipped with a UV-A lamp irradiating UV light between the wavelengths 320 and 400 nm directly on the sample, as shown in Figure 1. The oxidation and consumption of gas by the photocatalytic TiO_2 were determined by analyzing the absorption/reaction of NO_x, a gas representative of pollutants. Two additional components were used for this: a) a zero air generator (ZAG 7001) and a computerized calibrator (MGC 101) (both Environnement model) were used to adjust the initial concentration of the NO_x gas injected in the cell, and b) the environmental air monitor (Horiba) was used to recognize the input and output concentration of NO_x. The concentration of NO_x inlet was set at 1.2 ppm, since the same concentration has been used by other researchers performing similar NO_x degradation studies, and also because the usual concentration in several Brazilian environments (as stipulated by the Brazilian laws) are below this.[6] The flow rate was set at 0.7 L/min, and the test was carried out over a 50 min period. The performance of the samples was assessed over time of exposure to the gas and UV-A radiation.

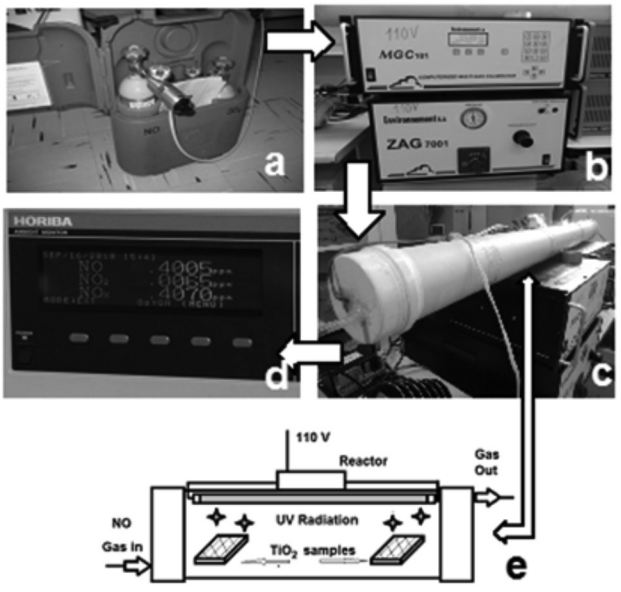

Figure 1. *Photocatalytic cell for the analysis of the gas: a) NO gas injector; b) equipment for the measuring gas consumption; c) in-house fabricated photocatalytic cell; d) gas in/out environmental air monitor; and e) schematic view of the analysis by photocatalytic cell*

RESULTS AND DISCUSSION

Specific results obtained from each experiment are presented and discussed below.

Materials characterization

The cement was characterized in accordance with the Brazilian standards and the results are listed in Table 3. The results indicate that the properties of the cement are in accordance to the ABNT standards and the recommendations of the manufacturer.

The characteristics of the natural sand, including its particle size distribution, indicate that it is suitable for use in mortar (Table 4).

XRD patterns of TiO_2 (Figure 2) indicate that the predominant phase is the anatase, which is considered to be photochemically active. From the high intensity diffraction peaks at 2θ values of 25° and 52°, the average grain size of crystallites is calculated to be 18 nm.

SEM micrograph of the TiO_2 powder is shown in Figure 3 and shows that the powder has a uniform texture with fine grains. EDS analysis indicates that the sample is predominantly composed of titanium and oxygen.

Photocatalytic tests

Figure 4 displays two results from the photocatalytic degradation of NO_x gas by the mortar samples with 10% TiO_2 (weight/weight).

Table 3. Physical, chemical, and mechanical characteristics of Portland cement, type CP II - Z 32

Properties	Test conditions	Results
Fineness (sieve residue)	# 200	2.6%
	# 325	8.8%
Blaine Fineness		3.790 cm^2/g
Cold Expansion		0.0 mm
Normal Consistency of Cement		26.4%
Specific Gravity		3.04 g cm^{-3}
Settling time	First	4 h 20 min
	Last	5 h 50 min
Compressive Strength	3 dias	23.0 MPa
	7 dias	26.4 MPa
	28 dias	32.8 MPa
Heat Loss		0.21%
Insoluble Residue		7.07%
Calcium Oxide		6.96%

Table 4. Mechanical and physical characterization of fine aggregate

Properties	Results
Fineness Modulus	2.46
Nominal Maximum Size	4.75 mm
Specific Gravity	2.52 g cm^{-3}
Unit Weight	1.57 g cm^{-3}
Water Absorption	0.4%
Soil content	0.3%

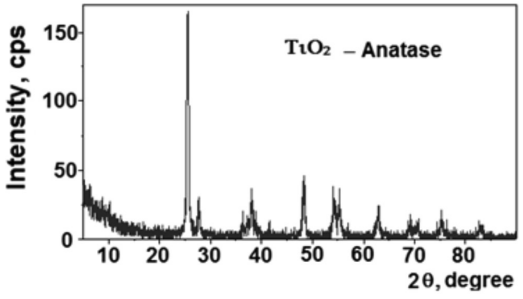

Figure 2. *XRD pattern of TiO_2-anatase powder*

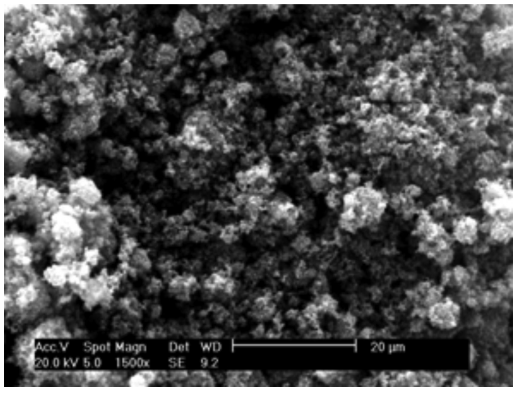

Figure 3. *SEM micrograph of TiO_2 powder surface (1500×)*

These measurements are conducted in the presence of NO_x gas (1.2 ppm) and UV-A radiation. Both samples present a 38 ± 1% reduction in NO_x gas during the ~35 min analysis period. The efficiency of the method can be viewed during the period the UV-A lamp is turned on. These results confirm that TiO_2 oxidizes the environmental pollutant, NO_x gas.

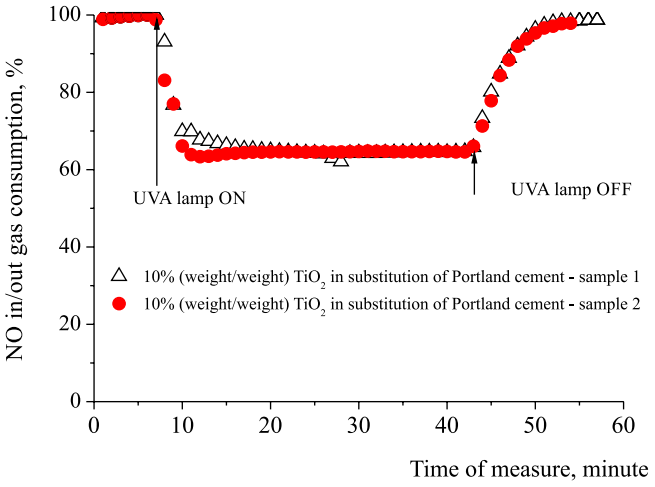

Figure 4. *Photocatalytic oxidation of NO gas under UV-A irradiation by mortar samples containing 10% TiO_2 (weight/weight; as Portland cement substitute) as a function of time*

The average results for oxidation of NO_x by mortar samples containing different concentrations of TiO_2 are shown in Figure 5. From the results, it can be noted that samples with different concentrations of TiO_2 mortar when irradiated by UV light are capable of oxidizing NO_x gas pollutants. When compared with the reference material (without TiO_2), 40% of the NO_x is photocatalytically degraded in the presence of mortar containing varying amounts of TiO_2.

The mechanism of photocatalytic oxidation of NO_x can be represented by Equations (1-9).[7]

$$TiO_2 + h_v \rightarrow e^- + h^+ \quad (1)$$
$$TiO_2 + H_2O \leftrightarrow TiO_2\_H_2O \quad (2)$$
$$TiO_2 + O_2 \leftrightarrow TiO_2\_O_2 \quad (3)$$
$$TiO_2 + NO \leftrightarrow TiO_2\_NO \quad (4)$$
$$H_2O_{abs.} \leftrightarrow OH^- + H^+ \quad (5)$$
$$h^+ + OH^- \rightarrow OH\bullet + H^+ \quad (6)$$
$$NO + OH\bullet \rightarrow HNO_2 \quad (7)$$
$$HNO_2 + OH\bullet \rightarrow NO_2 + H_2O \quad (8)$$
$$NO_2 + OH\bullet \rightarrow NO_3^- + H^+ \quad (9)$$

Equation (1) presents the absorption of photons (hν) of UV-A radiation by the semiconductor TiO_2, resulting in the transfer of an

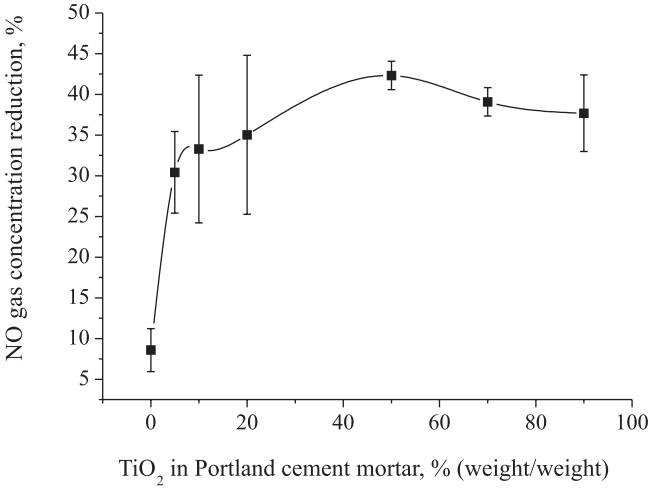

Figure 5. *Photocatalytic oxidation of NO gas under UV-A irradiation as function of percentage of TiO_2 in weight (as Portland cement substitute)*

electron (e^-) from the valence to the conduction band with generation of a hole h^+ in the valence band. The equations (2-4) show the adsorption of the reagents H_2O, O_2, and NO by TiO_2. The water molecules adsorbed on the surface of the semiconductor generate hydroxyl radicals (OH•), as demonstrated in the equations (5 and 6). Subsequently, these radicals are involved in the oxidation of NO and NO_2 to NO_3 (Equations (7-9)). Thus, the nitrates ions are the degradation products of NO_x.

It is evident from the graph that the higher rate of NO_x degradation is observed when there is a 30–50% content of photoactive material. It is not environmentally suitable and financially feasible to use larger volumes of material.

CONCLUSION

A method to evaluate the photocatalytic efficiency of TiO_2 for the oxidation of pollutants, such as NO_x gas, is developed. When a layer of the mortar containing 30–50% TiO_2 is irradiated under a UV light, up to 40% of NO can be reduced.

Besides, incorporation of photocatalytic agents in the mortar for the construction of various concrete artifacts is a very promising technique for minimizing pollutants, which can used on different objects, such as in electric poles for power distribution.

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