PERFORMANCE OF SELF-CLEANING COOL CEMENTITIOUS SURFACE

Ana Paula Werle*[1], Vanderley M. John[2], Kai Loh[3], Rômulo Ando[4] and Michele Lemos de Souza[5]

1 University of São Paulo
School of Engineering
São Paulo, Brazil
**ana.werle@lme.pcc.usp.br*

2 University of São Paulo
School of Engineering
São Paulo, Brazil

3 University of São Paulo
School of Engineering
São Paulo, Brazil

4 University of São Paulo
Chemistry Institute
São Paulo, Brazil

5 University of São Paulo
Chemistry Institute
São Paulo, Brazil

ABSTRACT

A strategy to reduce global warming is to increase the reflectance and thermal emittance of the built environment (Akbari, Menon, e Rosenfeld 2008). The urban heat islands usually increase the temperature by more than 10ºC (Santamouris et al. 2001). A cool roof can reduce the temperature up to 3.3ºC (Synnefa, Santamouris, e Akbari 2007) and improve indoor thermal comfort and reduce energy consumption. A comfortable indoor temperature in the buildings represents a better quality of life for those who cannot afford air conditioning besides reducing the cooling energy, costs and environmental impacts.

Most horizontal surfaces in cities are constituted by roofs and pavements and even cool when exposed to natural environment, degradation of these surfaces can occur due to factors such as UV radiation, wind and rain, biodeterioration and soiling.

Cool roofs and cool pavements constitute most of the horizontal surfaces in cities and interfere with the urban climate. The environmental exposure can cause degradation of these surfaces due to factors such as UV radiation, wind and rain, biodeterioration and soiling. Biodeterioration and soiling can be partially controlled by periodical cleaning but this procedure is time consuming, expensive and wastes water and detergents; moreover, roof cleaning is only possible when the surface is accessible and this is not always possible. Therefore, the best solution is a durable self-cleaning cool surface.

The aim of this research is to develop a durable self-cleaning cool cement-based surface. Three samples of TiO2 (anatase) products (P25, US NANO - IV and Millenium – TiONA) - added to cement pastes for self-cleaning solution - were studied. All the samples were characterized by X-ray Fluorescence Spectroscopy (XRF), while other tests focused on the measurement of the photocatalytic activity of TiO_2, using Congo Red dye on white cement paste specimens. 5% and 30% of TiO_2 were added, and the paste without addition was used as a reference. The changes after 5h of UV exposure were measured by surface analysis using absorbance measurements with UV-VIS Spectrophotometer, Raman Spectroscopy and Scanning Electron Microscopy, with EDS. The results showed that cement paste with addition of TiO_2 degrades the Congo Red dye more than the reference one and degradation is a function of the availability of TiO_2 on the surface.

Keywords
Self-cleaning, cementitious surface, TiO_2, Congo Red dye, photocatalytic degradation.

1 INTRODUCTION

TiO_2 (anatase) nanoparticles have been of interest due to their capacity to generate functional surfaces. When activated by UV radiation, TiO_2 is capable of oxidizing pollutants (Chen e

Poon 2009a; Destaillats et al. 2012; Janus et al. 2008), has biocide effect (Gumy et al. 2006), and concurrently generates self-cleaning inorganic surfaces (Aïssa et al. 2011).

It is clear that self-cleaning surfaces can reduce the cleaning process, lower maintenance costs and are associated to environmental impact. Commercial applications include self-cleaning glasses (Chabas et al. 2008; TX ACTIVE® 2006; Yu et al. 2006) and cement-based surfaces (Aïssa et al. 2011; Chen e Poon 2009b; Chen, Kou, e Poon 2011; Hüsken, Hunger, e Brouwers 2009). Research interest includes long-term performance of cement-based materials (Maury e De Belie 2010), special application on large cementitious surfaces, such as pavements (Chen, Kou, e Poon 2011) and also capability to degrade atmospheric pollution (Ai et al. 2011).

There are several anatase nanoparticle products in the international market. These products have different characteristics, including mineralogical composition, particle size distribution and surface area (Hussain et al. 2010). A systematic comparison among thirteen different samples showed significant differences in the inactivation of E coli bacteria (Gumy et al. 2006). However, a comparison of different anatase products performance when mixed with cement is not yet available.

Our objective wass to study three different TiO_2 anatase types from the market added to white cement paste and compare their performance to produce cement-based cool photocatalytic surfaces.

2 METHODS

The tests were divided into characterization of TiO2 powder by X-ray Fluorescence Spectroscopy (XRF) and quantitative measurements of the photocatalytic effect of TiO_2, added into white cement paste, using Congo Red (CR) dye. The degradation was measured by Absorbance with Spectrophotometer Shimadzu UV-VIS, Scanning Electron Microscopy (SEM) and Raman Spectroscopy.

The cementitious pastes were produced adding TiO_2 (0%, 5% and 30%) and water to white cement powder. The content of 5% of TiO_2 was defined based on the literature (Diamanti, Ormellese, e Pedeferri 2008; Aïssa et al. 2011; Lucas, Ferreira, and de Aguiar 2013) and the 30% content was defined so as to have an excess of TiO_2 in the specimens. Ø 25mm x h 2mm specimens were cast with the mixtures and cured for 24 hours in high humidity environment and dried at 40 ° C in oven, for 7 days;

2.1 X-RAY Fluorescence Spectroscopy (XRF)

Bulk semi-quantitative chemical composition was carried out in 3 samples of TiO_2 powder, by standardless XRF (Axios Advanced, PANalytical) from fluorine to uranium in glass samples. Loss of ignition was carried out at 1.050°C by 1 h.

2.2 Photocatalytic activity of TiO_2 using Congo Red (CR) dye degradation

The activity was determined by CR dye degradation, after 5 hours of UV radiation exposure.

The cementitious specimens, with TiO_2 additions, adsorbed CR dye (solution of 7 mg / L) on the surface. The specimens were in contact with the dye for 1 h, in constant stirring, in an environment protected from light. After this period, the specimens were washed with deionised water, without abrasion, to remove the possible excess of dye on the surface, and dried in an oven (40°C) for 2h.

The degradation test was carried out in a ventilated chamber with a source of UV radiation (Phillips lamp HPL-N 125 W high pressure mercury bulb with no glass). The specimens were placed on a glass base, at a 10cm distance of the UV radiation source for 5h. The experiment was monitored over time, with intervals of 1 hour. The specimens were removed from the chamber after each hour and the absorbance was measured in a spectrophotometer. Absorption changes were measured using integrating sphere, in which the reflectance data were transformed into absorbance using the Kubelka-Munk equation. Beam size at openings (at 20 nm slit width): Nearly 7 mm wide, 9 mm high - reflection side. Detectors:

photomultiplier and PbS cell. Through this procedure, it was possible to determine, in visible range (400-700nm), changes in colour after UV exposure time.

2.2.1 Absorbance Measurements

The measurements were performed with Spectrophotometer Shimadzu UV-3101 PC, in UV and Visible range (200 – 800nm).

2.2.2 Scanning Electron Microscopy with EDS (SEM)

SEM was performed on cement paste specimens, with 0% and 5% of TiO_2. The specimens were dried at 40 ° C for 48h. After dried, they were metallized with carbon in a Bal-tec Leica, Model SCD-050 and tested in the equipment FEI - Quanta600 EGF.

2.2.3 Raman Spectroscopy

RS was carried out on cement paste specimens; the measurements were performed at room temperature using a wavelength of 647.1nm in a Spectra Physics Kr + ion laser. The scattered light beams were analysed with Raman Dilor XY spectrometer, equipped with optical multichannel charge-coupled devices, with liquid nitrogen cooled detector.

3 RESULTS AND DISCUSSION

3.1 X-RAY Fluorescence Spectroscopy

The results of X-Ray spectroscopy are focused on Cl and SO_3, the main constituents detected in the test are presented in Table 1.

Table 1 Main elements identified in the chemical analysis of TiO_2 P 25 Degussa, US NANO, Millenium and LPC samples.

Components	P25 – Degussa (%)	US NANO (%)	Millenium (%)
SO_3	Nd	0.37	0.31
Cl	0.09	0.01	0.02
TiO_2	97.6	95.9	96.2
PF	2.23	3.14	3.01

nd = non detected compound

X-ray fluorescence results showed the presence of different components/elements in the samples. However, the amount of those components does not exceed 1% of the chemical composition of the material. U.S. NANO and Millenium samples have a considerable amount of SO_3, while the P25 sample presents a larger amount of Cl than the others. Such differences might be related to the products production route, which could have some influence on the products performance.

Most of the information about composition and structure of TiO_2 lies in the percentages of crystallite phases, as observed by Xu e Zhang (2009); León-Ramos et al. (2010); Hussain et al. (2010). According to the literature, the crystallographic characteristics are more important than the chemical analysis for photocatalytic activity. However, this test was performed to verify whether the impurities detected could influence photocatalytic performance.

3.2 Absorbance Measurements

The test was performed in three specimens of each formulation and showed similar results; thus, only one result was presented. Specimens containing TiO_2 addition present much more higher absorption in UV wavelengths fraction as compared to the reference specimen (figs. 1 and 2). The difference between the specimens in the UV spectrum is a function of the amount of TiO_2 added to the cement paste. Specimens with 30% TiO_2 in the mixture absorb a higher percentage of UV radiation as compared with the 5% addition. Data demonstrate the availability of TiO_2 for photocatalytic activity. In visible range, the behavior is the same for all samples with absorbance ratio of 0.01, or 99% reflectance.

The absorption of UV radiation test shows that each TiO_2 sample provides a specific absorption band, i.e., a unique absorption profile. The differences in profile could be attributed to the chemical composition of each product and result from the difference in elements on the surface of the particle.

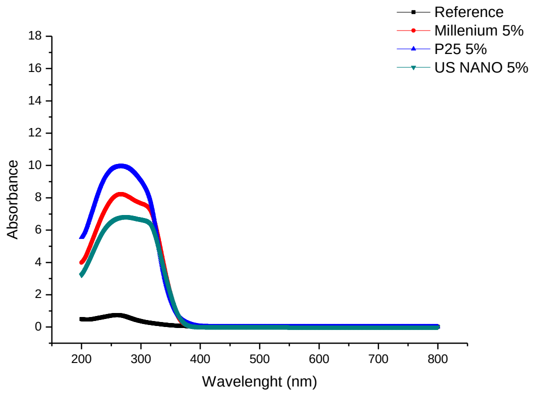

Figure 1 – Absorbance results for reference and paste with 5% TiO2

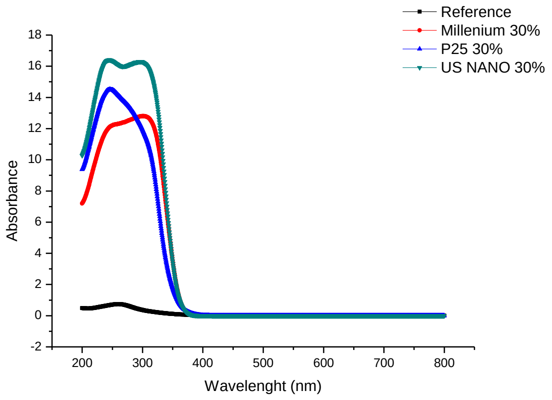

Figure 2 – Absorbance results for reference and paste with 30% of TiO2

3.3 Scanning Electron Microscopy (SEM) with EDS

SEM with EDS mapping is not usual to verify TiO_2 particles in self-cleaning solutions. This technique is a useful tool for checking TiO_2 availability on the surface. Fig. 1 shows the image of cement paste with 0% addition of TiO_2. Figs. 2, 5 and 6 show images of cement paste with 5% addition of $TiO_{2,}$ from three different products. The analysis was performed in three different spots of the specimens in each sample. Fig. 3, 4, 7 and 8 are the EDS spectra which show the components present on the specimens surface. The test shows the availability of TiO_2 on the surface and also shows the distribution of these particles. Only specimens with 5% TiO_2 addition were tested because this content is a more problematic scenario. The surface of the specimen is mostly covered by $CaCO_{3,}$ from cement carbonation (blue spots/dark color) and by TiO_2 (yellow spots/bright colors). Hence, if only 5% of the TiO_2 added to the cement paste was sufficient to identify TiO_2 on the surface, it is possible to assume that specimens prepared with 30% of TiO_2 will have much more of these particle available on the surface.

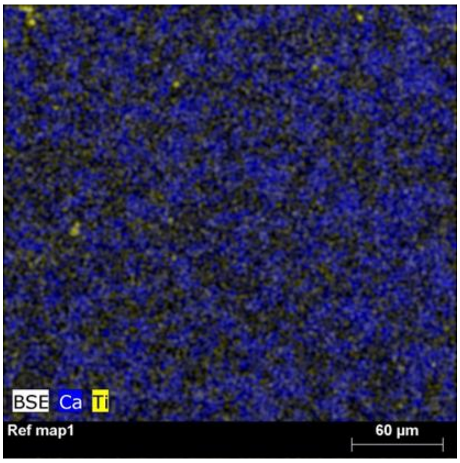

Figure 1 - Reference Sample - White cement

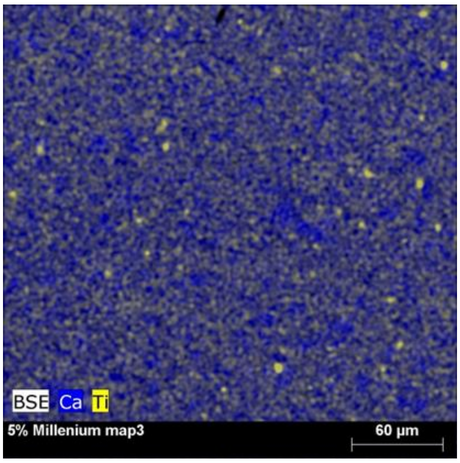

Figure 2 - Sample - White cement + 5% TiO_2 Millenium

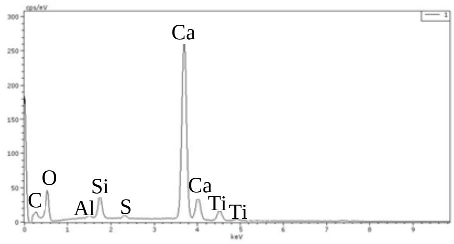

Figure 3 - Components present in the reference sample with white cement

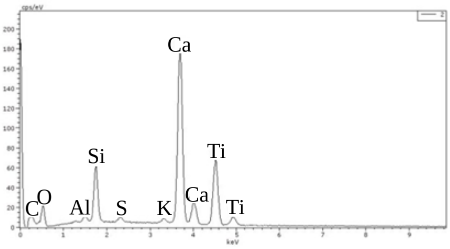

Figure 4 - Components present in the sample with white cement + 5% of TiO_2 Millenium

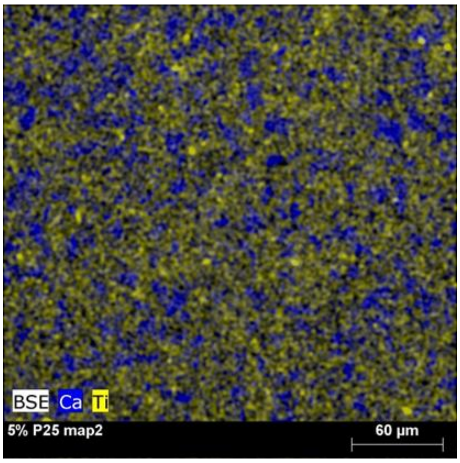

Figure 5 - Sample with white cement + 5% TiO_2 P25

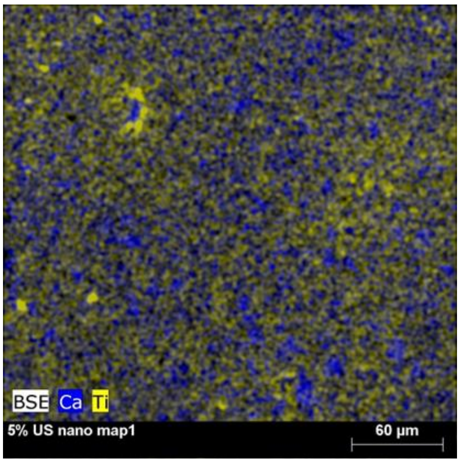

Figure 6 - Sample with white cement + 5% TiO_2 US NANO

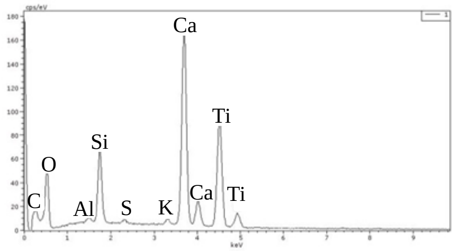

Figure 7 - Components present in the sample with white cement + 5% TiO_2 P25

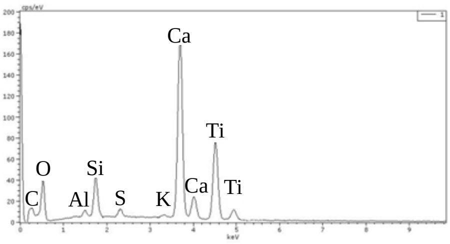

Figure 8 - Components present in the sample with white sample + 5% TiO_2 US NANO

3.4 Raman Spectroscopy

The crystallographic phases found on the specimens surfaces were calcium carbonate, liberated from cement hydration and carbonation phenomena, identified at 714 and 1087 cm^{-1} band, hydrated compounds, such as C-S-H (988 cm^{-1}) and ettringite (850 cm^{-1}). The same peaks were found by Deng et al. (2002); the authors also identified the hydrated cement compounds by Raman spectroscopy, which agrees with the peaks identified in this work, such as C-S-H, ettringite and $CaCO_3$.

TiO_2 samples exhibited a similar feature by Raman, peaks 395, 514, and 640 cm-1 bands, corresponding to the Raman fundamental modes of anatase phase (Li et al. 2011); however, the samples in this study showed peaks with distinct intensity. This evidences that each product has its own surface particle characteristics.

Raman spectroscopy makes clear how different the spectra of the specimens that have TiO2 in the mixture are when compared with the reference specimen. The reference specimen presents a characteristic and intense peak of calcium carbonate in the 1087 cm^{-1} band while specimens with TiO_2 present the same peak, but much less intense. Raman spectroscopy profiles are shown in fig. 9.

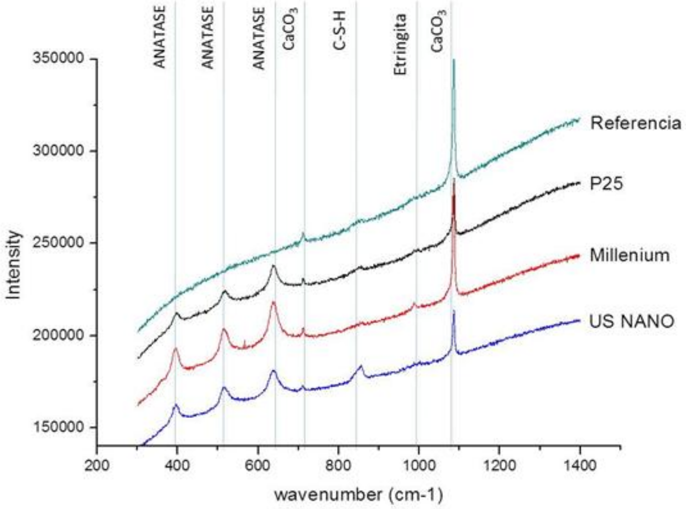

Figure 9 - Identification of elements over the sample surfaces by Raman Spectroscopy

3.5 Congo Red (CR) Dye Degradation

The dye degradation represents the photocatalytic activity of specimens containing TiO_2 comparatively to the reference. After 5h of exposure to UV radiation, the pastes prepared with 5% TiO_2 were observed to present more data variation and results of paste with TiO_2 and reference are very close to each other.

Specimens mixed with 30% TiO_2 present greater degradation than specimens with 5% TiO_2 showing that additions of over 5% are necessary.

Considering the final absorbance (300min of exposure) with 5% and 30% TiO_2 additions, it can be observed that absorbance reduced in the order of 8% for sample Millenium, 28% for US NANO and 94% for P25 and the reference presented 2%, 23% and 57%, respectively of absorbance decrease.

Results show the efficiency of the amount of product added to the mixture, as well as the efficiency of the P25 product for photocatalytic activity.

Da Costa, Zamora, e Zarbin (2011) studied the effect photocatalytic of different samples of TiO2, including P25, to degrade Reactive Blue-19 dye in solutions. The dye solution was observed to degrade 99% in the visible spectrum, with P25, after 60 minutes of UV radiation exposure. The equipment used was an UV-VIS Spectrophotometer, similar to the equipment used in this study.

Devi, Murthy, e Kumar (2010) studied the TiO_2 photocatalytic effect using aqueous solution of Congo Red dye, exposed to natural UV radiation. The degradation of the dye was measured with UV-VIS equipment in the visible spectrum (400 - 700nm). The authors showed that after sun exposure, the sample anatase doped with V, Zn, present higher photodegradation (38% to 100%) than undoped anatase and sample P25 presented photodegradation of 06% to 18%, respectively.

Janus et al. (2008) tested samples of artificially modified TiO_2 (doped with carbon nanotubes) and samples of P25. For the P25 sample, after 5.5 hours of UV radiation exposure, 100% of degradation of the mono azo dye was verified. The test shows that the two samples have equivalent performance in relation to photodegradation. The TiO_2 modified dye degradation occurred after 5h, while for P25 the dye degradation occurred after 5.5h.

The results of Congo Red dye degradation is presented in Figs. 10 and 11.

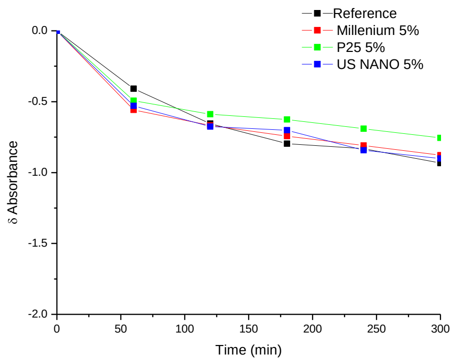

Figure 10 – CR dye degradation with 5% TiO2 in the matrix

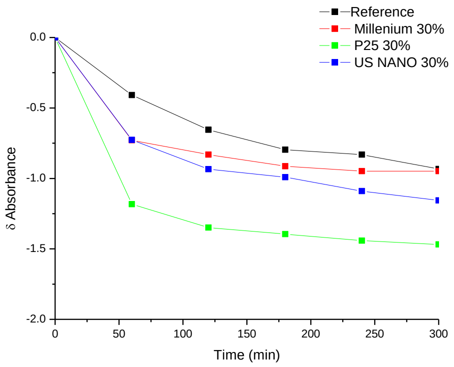

Figure 11 – CR dye degradation with 30% TiO2 in the matrix

4 CONCLUSION

The XRF test confirmed that each of the 3 samples of the study has a specific chemical composition.

SEM with EDS showed that there is TiO_2 available for photo catalytic activity on the surface of the white cement specimens and that these particles are quite well distributed on the surface.

Raman spectroscopy identified the crystalline phases of TiO2 and products of cement hydration and carbonation on the surface of the specimens as well as C-S-H and etringite.

Photocatalytic activity, verified by Congo Red dye degradation, demonstrated that the paste with TiO_2 addition exhibited higher degradation than the reference samples. Specimens with 30% TiO_2 in the paste degrade more than the specimens with 5% due to the greater availability of TiO_2 on the surface. The different types of TiO_2 have different degradation performance. Such differences can be attributed to the specificities of the products, such as different chemical elements or contents. In the experimental conditions of the P25 study, TiO_2 showed the best performance when compared with the reference, Millenium and U.S. NANO, when added to the paste at 30%.

The literature revue showed that UV–VIS spectroscopy is a very common and precise method to quantify dye degradation. However, there is still no consensus about the most appropriate type of dye for test procedures. Along the same lines, research is showing testing methodologies in aqueous solution. Nevertheless, this situation does not represent the scenario of TiO_2 application for building materials, with air purification and self-cleaning solutions. The procedure used in this study permitted to select the more photoactive TiO_2 sample showing that the test performance using cement paste is appropriate for TiO_2 photocatalitic studies for application in building surfaces.

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