TiO_2 and SiO_2-TiO_2 coated cement : comparison of mechanical and photocatalytic properties

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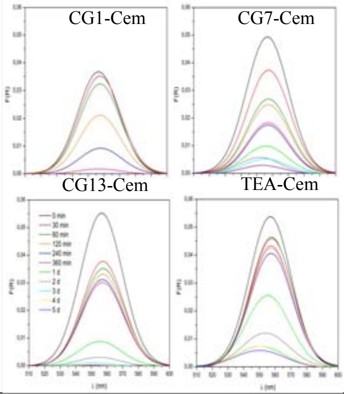


Despite regulation straightening, air pollutants concentration is one of the biggest problems that modern society faces, increasingly aware of the danger associated. Solar assisted heterogeneous photocatalysis has become an interesting alternative to degradate NOx and VOCs.

In this context, the photoefficiency of four TiO_2 coated cements (TiO_2-Cem) in Rhodamine B (RhB) and NO_x photodegradation tests and the effect of a SiO_2 interlayer (SiO_2-TiO_2-Cem) on the mechanical and photocatalytic properties has been analyzed. Although a good photodegradation was always achieved, the home-made titania (TEA) showed the best global behavior in both series.

Air quality has gone continuously degrading along last century due to high population, industrial activities and transportation that caused the urban air pollution [1]. Despite regulation straightening [2], air pollutants concentration is one of the biggest problems that modern society faces, increasingly aware of the danger associated. Solar assisted heterogeneous photocatalysis has become an interesting alternative in air pollution control to degrade NO_x and VOCs.

During last decades the development of new photoactive building material has woken up an enormous interest among urban communities, but advances slowed down after titania was introduced in different ways (spraying, mixing, intercalation, etc.) [3] and the effect of multiple reaction parameters was evaluated [4].

Nowadays the target is to obtain more active photocatalyst and more stable when applied over urban infrastructures to assure the durability and reduce maintaining costs. Commercial sprayable photo-catalytic suspensions contain some additives to guarantee the perdurability, but sometimes a detrimental effect over photocatalyst properties is consequently caused.

In this scenario, the analysis of some TiO_2 coatings photoefficiency and the effect of a SiO_2 pre-coating on the mechanical and photocatalytic properties were proposed. Four TiO_2 suspensions (three commercial and one home-made) coated cements (TiO_2-Cem) have been evaluated on RhB and NO_x photodegradation tests. Another series was previously sprayed with SiO_2 suspension and then TiO_2 coated (SiO_2-TiO_2-Cem), and the modification produced on mechanical and photocatalytic behavior was analyzed.

Cement mortar was constituted by cement: sand: water in 1: 3: 0.5 ratio. Samples were cured for 28 days on a chamber under saturated humidity environment. Commercial TiO_2 suspensions were supplied by Cristal Global: S5-300A (CG1), PC-S7 (CG7) and S5-300B (CG13), and homemade titania sol (TEA) was prepared by titanium isopropoxide hydrolysis in acid media and further purification by dialysis treatment. SiO_2 suspension was prepared in lab by hydrolysis of tetraethylorthosilicate in acid media. Suspensions were sprayed over mortar surface and dried at room temperature.

Physico-chemical properties of TiO_2 and SiO_2 suspensions, TiO_2-Cem and SiO_2-TiO_2-Cem samples were studied using various techniques (XRD, UV-Vis, ICP-OES, N_2-Isotherms, NH_3 chemisorption, SEM, SEM-BSE, TEM, etc.).

Table 1. Main physico-chemical properties of TiO_2 catalysts

	pH	TiO_2 (wt%)	S_{BET} ($m^2 \cdot g^{-1}$)	$d_{anatase}$ (nm)	Band-Gap (eV)
CG1	1	20	341	7	3.38
CG7	7	10	251	9	3.39
CG13	13	18	322	8	3.35
TEA	3	20	328	4	3.72

Photocatalytic activity for RhB (10^{-4} M) test was carried out in a closed chamber with 4 BLB (λ_{max}=360 nm) and 2 Daylight fluorescent lamps. RhB photodegradation was followed by UV-Vis diffuse reflectance at different time intervals along five days. NO_x photodegradation runs were carried out in a tubular photoreactor system that follows UNI 11247:2010 requirements.

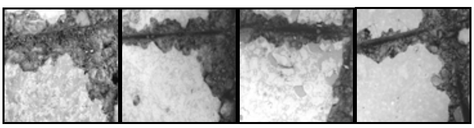
From XRD results, the commercial TiO_2 presented anatase mean crystal sizes between 6.6-8.6 nm, while the homemade TEA was constituted by smaller anatase crystallites (3.8 nm). Meanwhile, dolomite, calcite and anatase were the main crystal phases observed in the studied coated cements (TiO_2-Cem and SiO_2-TiO_2-Cem).

All TiO_2 catalysts presented very high surface areas (>300 $m^2 \cdot g^{-1}$) that could provide enough adsorption sites to better photocatalytic performance.

The layer thickness and interactions between TiO_2-Cement and SiO_2-TiO_2-Cement were analysed by SEM-BSE; although the commercial TiO_2 were deposited in a thicker layer, they were discontinuous and heterogeneous, by contrast, TEA coating was thinner but continuous and homogeneous; besides the images point out that some kind of interaction could be taking place. The interspersion of a SiO_2 layer produces a decrease in the thickness of TiO_2 coatings; even more, a fusion of SiO_2 and catalyst layer was observed when acid TiO_2 (CG1 and TEA) was spread.

From TiO_2-Cement adhesion test (Figure 1), CG1-Cem showed a very poor union between photocatalyst coating and cement support, even some scratches on cement surface can be observed, probably due to CG1 titania suspension acidity (pH 1).

On the contrary, CG7-Cem and, over all, TEA-Cem presented the best titania coating, with minimum peeling around cuts.TiO_2-Cement adhesion order was the following: TEA-Cem>CG7-Cem>> CG13-Cem>> CG1-Cem



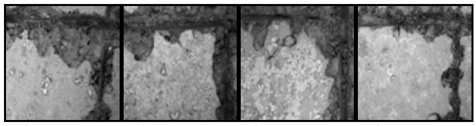
CG1-Cem CG7-Cem CG13-Cem TEA-Cem

Figure 1. Adherence test for TiO_2 coated cements.

In general, the SiO_2 sol coating does not seem to improve the durability of photocatalyst layer (Figure 2) compared to TiO_2 coated cements, except in the case of Si-TEA-Cem in which a close interaction between SiO_2 and TiO_2 was observed.

Thus, whereas Si-CG1-Cem presented a surface with multiple erosion and partial layer lost, intermediate adherences were observed for Si-CG7-Cem and Si-CG13-Cem. SiO_2-TiO_2-Cement adhesion order was the following:

Si-TEA-Cem >> Si-CG7-Cem >Si-CG13-Cem >>Si-CG1-Cem



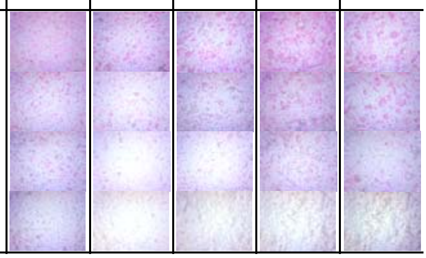
Si-CG-Cem Si-CG7-Cem Si-CG13-Cem Si-TEA-Cem

Figure 2. Adherence test for SiO_2-TiO_2 coated cements.

The good adhesion that TEA presented both with and without SiO_2 interlayer did not have a direct effect over photocatalytic efficiency, but taking into account the outdoor application, durability associated will be an appreciate property, avoiding the release of nanoparticles to environment.

As showed in Table 2, RhB photodegradation rate seems to be favoured by acid pH among commercial photocatalysts, probably due to RhB-TiO_2 interactions under or above titania PZC. Nevertheless, although TEA-Cem presented the slowest RhB photodegradation rate, all the studied photocatalysts achieved around 95 % of final conversion after 5 days.

Table 2. RhB photodegradation on TiO_2 coated cements (TiO_2-Cem).

	Cem	CG1-Cem	CG7-Cem	CG13-Cem	TEA-Cem
0 min					
1 h					
1 day					
5 days					

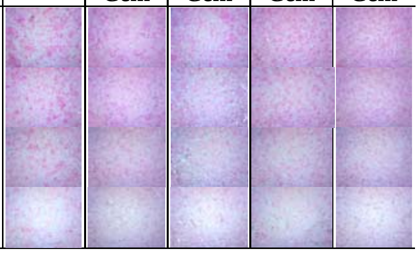
While, in Table 3, SiO_2-TiO_2-Cem results indicated that when a SiO_2 sol interlayer was applied the Si-CG1-Cem suffered a partial lost of efficiency, RhB degradation rate became slower, as happened to Si-CG13-Cem.

On the other hand, Si-CG7-Cem presented the fastest RhB photodegradation rate; meanwhile Si-TEA-Cem maintained the photoefficiency, although an initial activation stage is necessary, the maximum RhB conversion was reached after 5 days.

In parallel to the behavior of catalysts observed on RhB photodegradation, no significant differences among them were detected during normalized test of NO_x photocatalytic degradation under UNI 11247:2010 conditions. Molar conversions varied from 50 to 55% for the studied TiO_2 coated cements, which were enough high for the conditions of the test.

Table 3. RhB photodegradation on SiO_2-TiO_2 coated cements.

	Cem	Si-CG1-Cem	Si-CG7-Cem	Si-CG13-Cem	Si-TEA-Cem
0 min					
1 h					
1 day					
5 days					



It has to be remarked that the most active photocatalyst for one contaminant is not necessarily the most active for other contaminant.

Concluding from the obtained results, it could be pointed out:

The eight studied photocatalytic mortars showed a significative activity on RhB photodegradation.

SiO_2 layer between cement and photocatalysts did not stabilize the commercial TiO_2 coatings, whereas a good adhesion was observed when applied joint to TEA, probably because of the strong interactions between SiO_2 and TiO_2 sols.

Si-CG7-Cem showed high photodegradation rate at short irradiation times, but TEA-Cem and Si-TEA-Cem seemed to be the most promising photocatalysts due to an improved coatings adhesion.

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