Photocatalytic activation of textile reinforced concrete facade panels

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Abstract

Textile reinforced concrete (TRC) is an innovative high performance composite material which has been demonstrated to be a suitable material for façade panel solutions. These alternative reinforcement materials also offer a much lower density in comparison to steel reinforced concrete, which contributes to a reduction in dead weight. Resultantly, thinner, and thus lighter, façades made of TRC reduce the environmental impact from both the manufacturing process and subsequent transportation. The thinner dimension is also favorable to either increase the insulation thickness or to use different types of insulations. Further enhancements to TRC panels in the form of self-cleaning surface properties were investigated within the FP7 project H-HOUSE project. Photocatalytic properties using titanium dioxide (TiO_2), were focused on which, when activated by UV light destabilize hazardous compounds in the surrounding environment.

In this paper, incorporation methods related to various commercial TiO_2 products were particularly studied, such as bulk incorporation or surface treatment. The photocatalytic activity of the functionalized surfaces was evaluated using photocatalytic indicator ink which is chemically reduced under photo-induced reactions. Through surface analysis, it was found that the distribution of the TiO_2 when mixed homogeneously in a cement paste was highly dependent on the applied quantity, composition of TiO_2, and likely the paste composition. TiO_2 in the form of a dispersion can provide a superior reactivity rate when applied directly to the mould surface, at the expense of even and controllable surface distribution. A top coat of a TiO_2 solution onto the hardened concrete surface resulted in the most rapid and highest amplitude of surface colour change. These investigated incorporation methods proved to yield promising results in terms of the level of photocatalytic surface activation of TRC panels.

Keywords: Self-cleaning surface, Titanium dioxide (TiO_2), photocatalytic evaluation, textile reinforced concrete, façades

1. Introduction

Titanium dioxide (TiO_2) is known to be photocatalytic in the presence of UV light of a certain frequency, this was first shown by Fujishima [1]. Embedded on media and exposed to the right conditions, it is collectively known to create a so-called self-cleaning property leading to e.g. the decomposition and removal of air and water contaminants [2]. Typical examples of its use are windows, tiles and other surfaces exposed to UV light in the built environment. Within the FP7 project H-house (Healthier Life with Eco-innovative Components for Housing Constructions), the incorporation of this self-cleaning property is being evaluated for use on eco-innovative textile reinforced concrete building façades. The self-cleaning property is commonly incorporated as a part of the exterior facing panel itself or as a secondary surface layer. The production of a thin photocatalytic layer to be incorporated as a secondary layer to the façade was focused upon so as to generate an economic solution.

Complex assessment methods for the determination of photocatalytic activity typically involve the use of NO_x (model air pollutant) and isolation cabinets as described in e.g. *JIS R 1701-1* [3] or ISO 22197-1 [2]. A simpler and more rapid assessment procedure is also available which encompasses indicator inks along with weathering conditions. For example, the use of methylene blue (refer to DIN 52980 [4]) can be applied as a surface pollutant coupled with artificial UV radiation and water to determine the photocatalytic activity of surfaces. An alternative indicator ink is resazurin (Rz), available from e.g. *Ink Intelligent*, which has been shown to be a relatively reliable indicator of photocatalytic surface activity due to its irreversible colour reduction which is unlike the case for methylene blue [5]. Rz ink is initially blue in colour when applied to a surface and becomes a pink colour (resorufin, Rf) upon chemical reduction due to photoirradiation [6].

The aim of this study was to investigate the differences in the rate of photocatalytic activity of commercially available TiO_2 products. The application method was also studied, whereby bulk addition and surface applications where considered. Rz indicator ink was used to rapidly assess the reactivity of the treated surfaces. Various analysis methods, such as colour spectrum, time to bleach and surface analyses, were coupled to gain an understanding of the photocatalytic activity and distribution of the TiO_2 catalyst.

2. Experimental investigation

The experimental program focused on the evaluation of the photocatalytic activity of various commercial TiO_2 products according to incorporated quantity and application method. A rapid assessment procedure using Rz indicator ink from *Ink Intelligent* was applied to the treated surfaces. The rate of change of colour measured by capturing photos of the specimens after fixed exposure to UV-A light intervals indicates the photocatalytic activity and respective self-cleaning effect. These photos were thereafter converted digitally into numbers on the RGB (red, green, blue) scale (0-256) and compared to each other based on the normalised Red value in this case (Rt). Thereafter, the dispersion of the TiO_2 particles was investigated by using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

2.1. Materials

Three commercial TiO_2 products, as listed in Table 1, have been applied to provide a photocatalytic property to the external TRC panel surface of the sandwich elements being produced in H-House. The products studied consisted of varying amounts of TiO_2 content, of which was accounted for in the mixtures. Moreover, due to the differing composition of these TiO_2 products, various application methods were also investigated, such as bulk application (cement replacement) and direct application (on mould surface or hardened surface). Reference specimens without any photocatalytic agent were also included in the study as a baseline.

Table 1: TiO_2 product alternatives.

Product	**Producer**	**Description**	**TiO_2 content [%]**[*]
TiOmix® N	Cementa	A proprietary concrete addition based on cement, slag and TiO_2	30-70
AEROXIDE® TiO_2 P25	Evonik Corporation Silica	Hydrophilic fumed titanium dioxide (pigment)	≥99.50
AERODISP ®W 740X	Evonik Corporation Silica	Water-based dispersion of AEROXIDE fumed titanium dioxide with a very high solids content and slightly acidic pH value	39-41

[*] Stated as per manufacturer.

The photocatalytic property of these TiO_2 product alternatives was tested on thin specimens made of cement paste. This type of specimen is thought to be able to economically simulate an additional thin layer of so-called photocatalytic paste which could be applied on the surface of a TRC panel. The reference cement paste recipe consisted of 1353 g of Bascement (Cementa, CEM II A/V 52.5 N) and 547 g of water leading to w/c ratio of 0.4. Superplasticizer was not included to the high amount of cement used and hence a high water content. This amount of water in kg/m^3 was sufficient to obtain a workable paste. Previous trials involving the inclusion of TiO_2 (powdered form) proved problematic at higher replacement volumes, so this was avoided by the higher water content and resulting cement content.

All recipes underwent the same mixing sequence in a 1 l Hobart mixer with a paddle attachment. The total mixing time was 240 seconds. The various batches were cast into 25 mm x 25 mm x 3 mm moulds without the use of a demoulding agent. After each use, these moulds were placed in an ultrasound cleaner. Circa 24 hours after mixing, the specimens were demoulded and placed under water in a climate room (98 ± 2 % RH and 20ºC). Initial experiments carried out in this project had shown that early testing of the photocatalytic activity caused colouring issues with the testing ink whereby the Rz ink turned into a brownish colour. Testing with this particular indicator ink was found to be more effective six months after casting.

2.2. Method of incorporation

Four test series were included in this study (Test series 1 to 4), which encompass different TiO_2 products, concentrations and incorporation methods as summarized in Table 2.

Table 2: Experimental matrix with designated test series.

TiO_2 product	**TiO_2 content [wt.-%]**	**Test series**	**TiO_2 product replacing total binder volume [% vol.]**	**Volume of product**	**Method of incorporation**
TiOmix®N	50 (assumed)	1	0, 4, 8, 12, 16 (Case 0 to 4)	−	Bulk application
AERODISP ®W 740X	40	2	0, 2, 4, 6, 8 (Case 0 to 4)	−	Bulk application
		3	−	50, 100 µl	Applied to moulding surface
AEROXIDE®TiO_2 P25	≥99.50	4	−	15 g + 100 ml waterborne potassium and sodium silicate liquid	Applied to hardened surface

2.2.1. Bulk application

The bulk application of TiO_2 was investigated in both Test series 1 and 2. TiO_2 was incorporated into the reference cement paste by replacing a prescribed percentage of binder volume (see Table 2). The experimental matrix ranged from 0 to 16% replacement of the total binder volume with TiOmix® N (assumed 50 wt.-%. TiO_2 content), whereby the equivalent wt.-% of TiO_2 in the dispersion (AERODISP®W 740 X, 40 wt.-% solid content) was used to match the mix containing TiOmix® N. The mean equivalent wt.-% of TiO_2 in both matrices is 1.4% (Case 1), 2.9% (Case 2), 4.3% (Case 3) and 5.8% (Case 4), based on a particle density of 4230 kg/m^3. The corresponding cement paste recipes are presented for both Test series 1 and 2 in Table 3.

Table 3: The cement paste recipes used in Test series 1 and 2.

Test series	Material	Quantity [kg/m^3]				
1	Binder replacement [% vol.]	0 (Ref)	4	8	12	16
	Bascement CEM II A/V 52.5 N	1353	1312	1271	1228	1185
	Water	547	536	530	525	519
	TiOmix® N	0	55	110	167	225
2	Binder replacement [% vol.]	0 (Ref)	2	4	6	8
	Bascement CEM II A/V 52.5 N	1353	1341	1314	1287	1259
	Water	547	496	443	391	340
	AERODISP®W 740 X	0	68	137	205	273

2.2.2. Direct surface application

The direct surface application of TiO_2 was investigated in Test series 3 and 4, whereby TiO_2 was either applied as dispersion on the moulding surface or as a paint-like coating, respectively. More specifically, in Test series 3, a fresh coating of AERODISP®W 740 X with fixed volume (50 or 100 µl respectively) was applied directly to the mould surface (25 mm x 25 mm) without the addition of a demoulding agent. The mould was placed on top of a vibrating table whilst the dispersion was applied to allow for a more even spread. The reference cement paste was thereafter poured over the dispersion. As a part of Test series 4, a number of reference specimens were treated with a paint-like surface coating after six months of casting. This coating was produced by thoroughly mixing 15 g of AEROXIDE®TiO_2 P25 and 100 ml of a waterborne potassium and sodium silicate liquid (Controll®INNERSEAL, Maynor A/S). This mixture contained approximately 11 wt.-% of TiO_2. One coat was applied to the hardened surface of the reference specimens with a standard paintbrush. The paint solution was allowed to dry for seven days in a laboratory environment (20 °C and 30 % RH). Excess coating was removed with a 240 grit sand paper prior to applying Rz indicator ink and undergoing testing. At this point, the precision and efficacy of the application method (i.e. airbrush, doctor blading) was not further investigated.

2.3. Test methodology

The test methodology involved four main steps: 1) application of indicator ink to surface, 2) exposure of ink surface to UV-A light cycles, 3) capture surface colour changes using photography and 4) analyse the Rt colour change of the photos to yield effectivity and time to bleach values. For selected specimens, the concentration of TiO_2 on the surface were analysed using SEM paired with EDP.

As a part of Step 1, samples from each series were removed from the climate room and allowed to surface dry for approximately 30 minutes. The indicator ink, denoted as *The Explorer* from *Ink Intelligent,* was applied in three layers with an interval of ten minutes between each coat. Four samples from each series plus a reference were positioned on the testing platform so that each was exposed to the same amount of radiation energy. Photos of the initial samples were taken prior to the beginning of experimentation. The samples were exposed to 180 seconds of radiation energy and then removed for further photography. This cycle was carried out until the total exposure time had reached 1800 seconds, amounting to ten cycles in total.

The experimental rig used to expose the specimens in Step 2 consisted of a single 300 W OSRAM Ultra-Vitalux bulb with a vertical distance of 0.5 m to the testing surface. The variation of the radiation energy hitting the specimens was also taken into account after the testing area was measured. The actual UV-A light hitting the testing surface measuring approximately 100 mm x 140 mm was measured at a number of points depicted in Figure 1. The difference in the amount of energy registered on the sensor with and without a glass covering was noted. The area to the left of “2I” and “2II” were deemed the edge of the radiation window an average value of 21.7 mW/cm^2 was used (see Table 4).

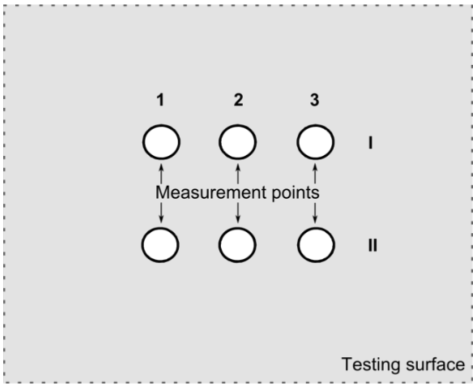

Figure 1. Measurement points of light energy.

Table 4. Light radiation measurements at measurement points on testing surface.

Area	Total light energy		Without UV radiation		UV light		Units
	I	II	I	II	I	II	
1	30.0	36.2	19.3	23.3	**10.7**	**12.9**	[mW/cm^2]
2	67.6	67.0	46.0	45.2	**21.6**	**21.8**	
3	71.5	67.6	50.2	45.5	**21.3**	**22.1**	

The RAW images taken during the experimentation in Step 3 were processed in an open-licensed software, *ImageJ* [7] as a part of Step 4. The images of each specimen from 0 to 1800 seconds were stacked upon each other digitally. Each series had four samples; these were converted to RGB scale. The data was exported to MS Excel and further processed so that each time interval of each sample was normalised to the red value (Rt). The average value of Rt obtained for each sample from a test series at the same time interval was then plotted against the corresponding time interval (in seconds). Further information pertaining to this evaluation method is reported in [7].

3. Results and discussion

The results obtained from exposing the various treated surfaces to UV light were further analysed using: 1) colour spectrum analysis, 2) time to bleach analysis and 3) surface analysis (SEM & EDP).

These analyses methods essentially enabled a comparison between the different TiO_2 alternatives according to normalized values.

3.1. Colour spectrum analysis

The colour spectrum analysis consists of the determination of the rate of colour change of the indicator ink from blue (Rz) to pink (Rf) due to chemical reduction caused by photoirradiation. The red colour (Rt) is of particular relevance which was digitally extracted from the photographs taken after each exposure cycle (refer to Section 2.3). An overview of colour change captured through stacked photos from 0 to 1800 seconds is depicted in Figure 2 for Test series 1 (top) and Test series 2 and 3 (bottom). For Test series 1, the most significant average colour change was observed for 8%, while the mould surface application investigated in Test series 3 appeared to be the most reactive of all variations using AEROXIDE®W 740 X. The 4% specimens appear to have undergone the most average colour change for Test series 2.

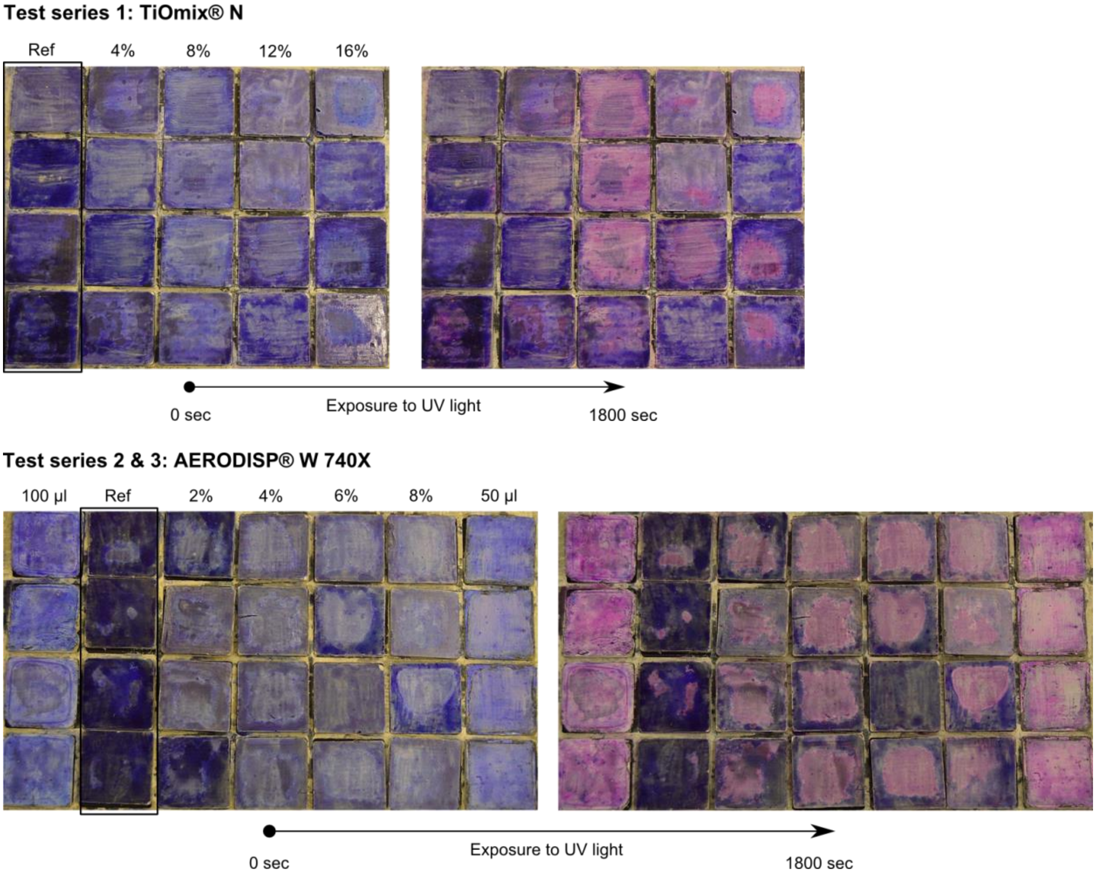

Figure 2. Specimens before and after exposure to UV light (0-1800 seconds): Test series 1 (Top) and Test series 2 and 3 (Bottom).

Furthermore, the normalization of the Rt colour spectrum plotted against the elapsed exposure time can provide a clearer and comparative understanding of the so-called rate of colour change. It can be observed from Figure 3 (left), that the rate of change for the TiOMix® N specimens tend towards that of the reference specimens. As previously noted, the specimens with 8% are confirmed to have the most effective rate of colour change. Concerning Test series 2, the bulk application of AEROXIDE®W 740 X tend towards the results obtained for Test series 3, as shown in Figure 3 (right). A rather minimal improvement in the rate of reaction is noted for specimens with 2, 6 and 8% volume replacement of binder. The specimens with 4% do however result in the most similar rate of reaction to that of 50 µl and 100 µl. From these findings, it appears as if the bulk application of TiOMix® N was less effective compared to AEROXIDE®W 740 X. Also, there was no clear relationship between the increase of TiO_2 and increase in rate of reaction. Since the concentration of the TiO_2 was assumed based on a wide range for TiOMix® N, it cannot be certain that it is only the effectiveness of the product which was the cause for the poor reactivity. Further surface analysis was therefore conducted using SEM and EDS as presented in Section 3.3.

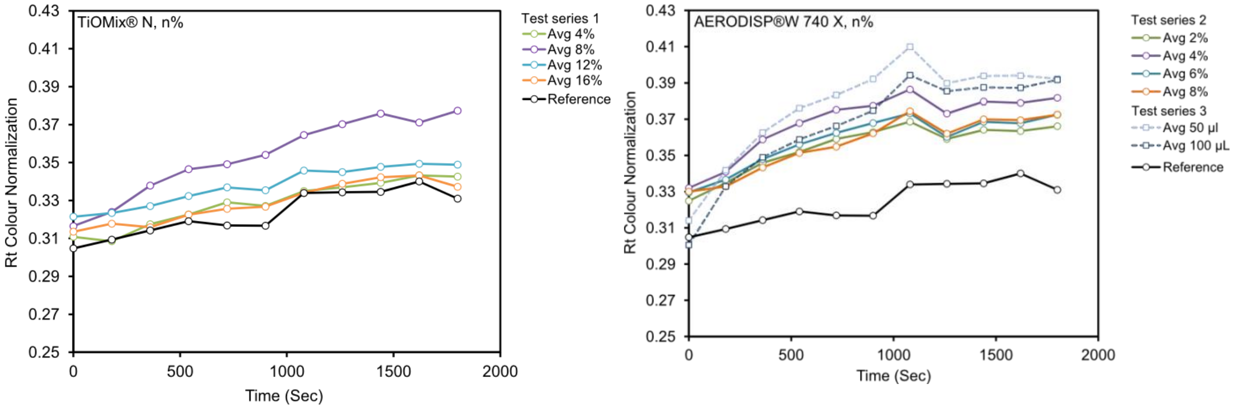

Figure 3. Average normalized Rt colour change of specimens with varying %-vol. replacement of binder with TiOmix® N (left) and AERODISP®W 740X (right).

The surface application in the hardened state, with the 11 wt.-% of TiO_2 solution, performed the best in terms of rate of reaction. One can even see that the background colour of the "pre ink" condition had returned in certain areas, see Figure 4. This grey colour is also processed into RGB values, as previously described in Section 2.3, leading to drops in the normalized Rt value as can be seen in Figure 5.

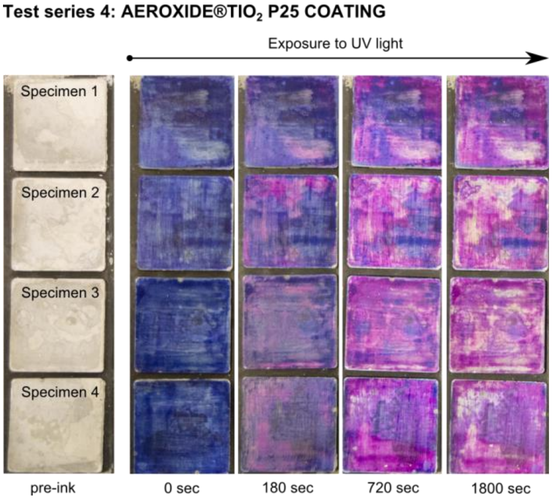

Figure 4. Test series 4 – AEROXIDE®TiO_2 P25 surface coated specimens before and after UV light exposure.

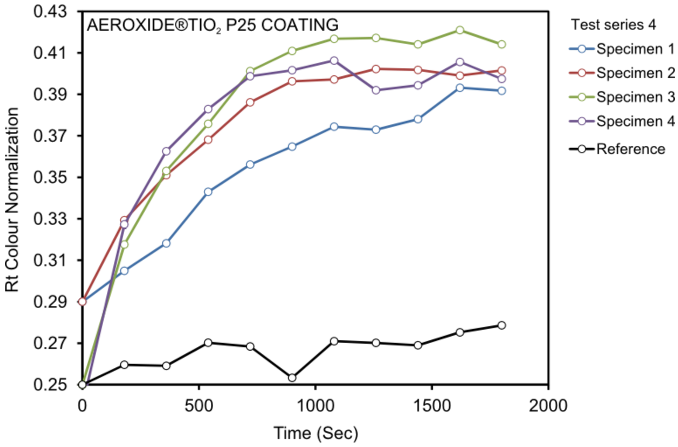

Figure 5. Normalized Rt colour change of specimens with AEROXIDE®TiO_2 P25 coating.

3.2. Time to bleach analysis

The information from the graphical depictions shown in Section 3.1 can be further manipulated in order to obtain the time to bleach (ttb). The ttb, measured as a unit of time, is essentially the point at which the slope of the rate of reactivity meets the horizontal slope of the reaction representing the drop off once it has reached its peak change. It is to say that the reactivity of the measured surface is quicker as the resulting time is lower. For further details pertaining to the analysis procedure for ttb, refer to [7]. Moreover, the interpreted average ttb for all test series and respective specimen variations are compared in Figure 6.

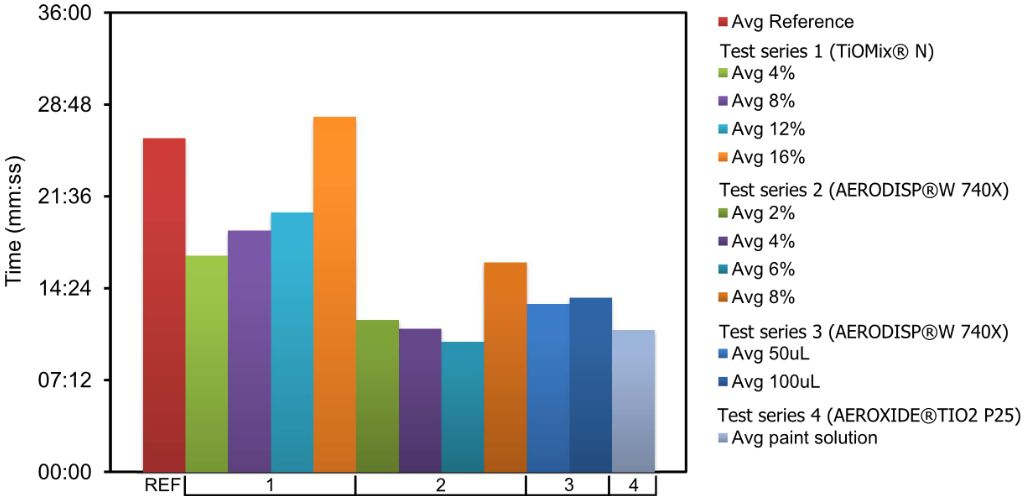

Figure 6. Average time to bleach (ttb) for all test series and specimen variations.

It is difficult to define the ttb due to the minimal slope change throughout the reaction for Test series 1; therefore a level of uncertainty exists in these results. For Test series 2, there is but a minimal difference between the ttb of 2%, 4% and 6% due to the fact that the initial slope of the rate of reaction follows a similar trend however the rate of reaction for 4% becomes slightly higher. For the cases which had superior rate of colour change, i.e. Test series 3 and 4, the change of colour occurred over a longer period of time thus causing the ttb to be slightly higher than the majority of results in Test series 2.

3.3. Surface analysis

The surface of the bulk application specimens (Test series “T” and “A”) were examined to determine the amount of TiO_2 that could be detected. Hydration products from the cement and water reaction resulted in a layer of $Ca(OH)_2$ (portlandite) being deposited onto the surface and thereby hindering chemical analysis with precision. The surfaces of one specimen from each series were sanded and polished until an even surface was obtained, as shown in Figure 7, and thereafter analysed using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Three specific areas were analysed from each sample to get a representative average of the elements found on the surface using EDS. The resulting quantitative analysis of the elements performed using EDS is summarized in Table 5 and
Table 6.

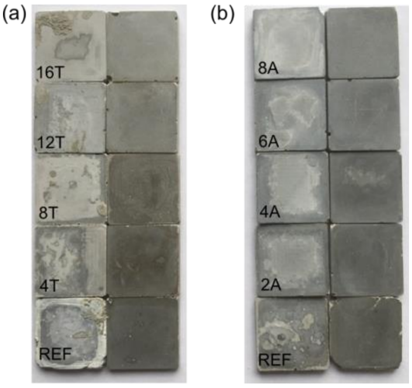

Figure 7. Test series 1 and 2 samples with denoted wt.-% of TiO2 of binder additive: a) TiOmix®N, "T" and b) AeroDisp®W 740X, "A". Samples on the right of each series are polished.

Table 5: Average results of EDS analysis of Reference and TiOmix® N surfaces.

Element	Average fraction [-]				
	Reference	TiOmix® N (Test series 1)			
	REF	4T	8T	12T	16T
Na_2O	0.2	0.2	0.5	0.1	0.1
MgO	3.4	3.4	4.2	3.0	3.3
Al_2O_3	7.6	8.8	7.3	7.2	7.2
SiO_2	29.6	30.3	23.2	27.8	27.9
SO_3	3.9	0.6	0.5	2.0	2.6
ClO	0.3	0.3	0.2	0.5	0.5
K_2O	0.3	1.2	1.8	0.5	0.3
CaO	50.3	48.4	54.3	48.1	45.3
TiO_2	**0.4**	**2.6**	**4.2**	**7.1**	**9.3**
Fe_2O_3	4.1	4.2	3.6	3.7	3.4
Total	100.0	100.0	100.0	100.0	100.0

Table 6: Average results of EDS analysis of Reference and AERODISP®W 740X surfaces.

Element	Average fraction [-]				
	Reference	AERODISP®W 740X (Test series 2)			
	REF	2A	4A	6A	8A
Na_2O	0.2	0.0	0.1	0.1	0.2
MgO	3.4	3.0	3.5	2.9	3.4
Al_2O_3	7.6	7.9	8.3	7.0	7.1
SiO_2	29.6	29.9	31.9	27.7	25.1
SO_3	3.9	3.1	2.0	3.1	1.9
ClO	0.3	0.4	0.4	0.2	0.3
K_2O	0.3	0.2	0.4	0.2	0.4
CaO	50.3	48.4	43.7	47.5	49.2
TiO_2	**0.4**	**2.8**	**5.5**	**7.5**	**8.8**
Fe_2O_3	4.1	4.3	4.2	3.9	3.6
Total	100.0	100.0	100.0	100.0	100.0

It can be observed from the EDS analysis results shown in Table 5 and Table 6 that the concentrations of TiO_2 in the two series noticeably increase as the wt.-% of TiO_2 increases. An increasing trend in TiO_2 concentration as the wt.-% increases should however also instigate an increase in surface reactivity, which was not apparent based on the colour spectrum and ttb analyses (Sections 3.1and 3.2). It is evident that the portlandite deposits on the surface interfere with the reactivity of the TiO_2.

Moreover, the estimated wt.-% of TiO_2 in both the Test series 1 and 2 specimens was found to be comparable, however a few discrepancies can be pointed out in Figure 8 (right) likely due to isolated concentrations of TiO2 pertaining to Test series 1, see Figure 8 (left). These clusters resulted in an increase in TiO_2 fraction particularly for the 12T and 16T samples. It can be established that there is a more effective surface distribution of TiO_2 in the Test series 2 samples (AERODISP®W 740X).

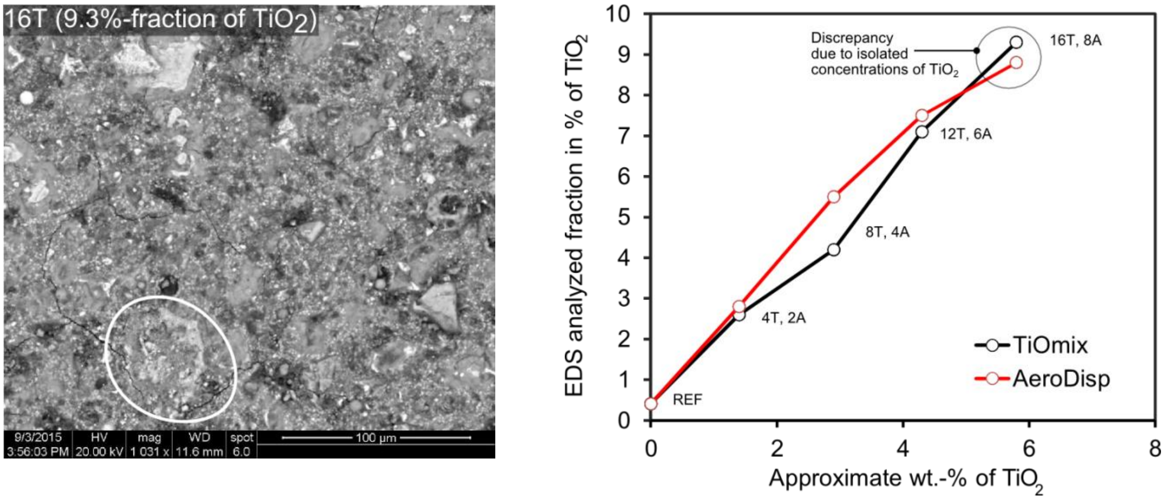

Figure 8. 16T sample image (x1000) with isolated concentration of TiO_2 (left) and EDS analysis of TiOmix® N versus AERODISP®W 740X (right).

4. Conclusions

The use of an indicator ink to determine the photocatalytic activation proved to be an effective and rapid test method. The colour spectrum and time to bleach analyses revealed that the application of higher amounts of TiO_2 into the cement paste did not directly result in a higher rate of photocatalysis or reduction in time to bleach. This phenomenon is thought to be due to the surface chemistry, so-to-say the precipitation of portlandite onto the surface preventing the activation of TiO_2, which was observed via SEM analysis.

An optimum amount was found in both the TiOmix® N and AERODISP® W 740X batches to be 8 % and 4 % binder volume replacement, respectively. These equate to the same TiO_2 weight content of 2.9 wt.-% based on the recipe. The surface reactivity of the specimens having higher binder volume replacement could have been improved with surface treatment prior to ink application. An increase in surface reactivity was however observed with an application of TiO_2 onto the surface of the cement paste (AERODISP® W 740X). The application of a coating onto the fresh paste moulding surface proved to allow for a superior surface activation, but the aesthetics were not satisfactory. The post-production application of a surface coating (11 wt.-% AEROXIDE® TiO_2 P25) resulted in the highest rates of reaction. It was so effective that localized areas of ink were completely degraded after maximum test exposure. Moreover, from a material cost point of view, the surface coating would be cheaper as the volume occupied by the coating is a lot less than in the bulk format and hence more cost effective.

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References

[1] Fujishima A. Electrochemical photolysis of water at a semiconductor electrode. nature. 1972;238:37-8.

[2] ISO 22197-1. Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for air-purification performance of semiconducting photocatalytic materials - Part 1: Removal of nitric oxide. Switzerland: International Organization for Standardization; 2009.

[3] Japanese Industrial Standard (JIS). Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for air purification performance of photocatalytic materials — Part 1: Removal of nitric oxide. JIS R 1701-1. Tokyo: National Institute of Advanced Industrial Science and Technology and Japan Fine Ceramics Association; 2004. p. 1-9.

[4] DIN 52980. Photocatalytic activity of surfaces - Determination of photocatalytic activity by degradation of methylene blue. 2008.

[5] Mills A, Wang J, McGrady M. Method of Rapid Assessment of Photocatalytic Activities of Self-Cleaning Films. The Journal of Physical Chemistry B. 2006;110(37):18324-31.

[6] Mills A, Hepburn J, Hazafy D, O'Rourke C, Krysa J, Baudys M, et al. A simple, inexpensive method for the rapid testing of the photocatalytic activity of self-cleaning surfaces. Journal of Photochemistry and Photobiology A: Chemistry. 2013;272:18-20.

[7] Hepburn J. Inkintelligent. INTEC RGB Extraction and Data Analysis. Retrieved: February 2015. http://www.inkintelligent.com/wp-content/uploads/2013/06/RGB_Extraction_Guide.pdf