Emissions Reducing Benefits of Multi-Functional Photocatalytic Concrete Inlays

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Abstract

Thin, multi-functional concrete inlays constructed with flowable fibrous concrete (FFC) and containing titanium dioxide (TiO_2) nanoparticles offer enhanced constructability and performance characteristics as well as environmental benefits, including the ability to reduce NO_x pollution in near-road urban environments. Photocatalytic FFC mixes incorporating different cement types and fly ash replacement were prepared in the laboratory to characterize NO_x removal ability and analyze the impact of factors such as carbonation and reflectance on photocatalytic activity. Highly reflective specimens containing white TiO_2 cement greatly enhanced photocatalytic efficiency compared to less reflective specimens made with gray TiO_2 cement. Carbonation of the concrete specimens significantly decreased photocatalytic performance, although mixes incorporating fly ash somewhat reduced the impact of carbonation on the photocatalytic efficiency. By quantifying the effects of different variables on photocatalytic performance, the results of this study can be used to optimize a photocatalytic concrete mix design to maximize NO_x removal under certain environmental conditions, NOx concentration levels, and carbonation.

Introduction

Pavement preservation has received increasing attention in recent years as a strategy to enhance pavement service life by addressing deterioration at an early stage and thus avoiding the need for larger-scale maintenance and rehabilitation. To date, preservation techniques and solutions used by agencies have predominantly incorporated asphalt cement products according to Peshkin et al. (2011). The desire for sustainable preservation options along with recent advancements in concrete technology have led to the development of newer concrete preservation solutions. In particular, the development of flowable fibrous concrete (FFC) mixes has allowed for the emergence of thin concrete inlays as a viable choice for pavement preservation.

FFC mixes combine the rapid constructability of self-compacting concrete (SCC) with a higher volume of synthetic macro-fiber reinforcement. Bordelon and Roesler (2011) demonstrated the constructability of an FFC mix for thin concrete pavement inlays through a full-scale test section and evaluated factors such as bonding to the underlying asphalt, panel size, and joint cracking. Additionally, the enhanced fracture properties and residual strength of the FFC mix were verified in laboratory testing.

In addition to offering improved constructability and structural properties, thin FFC inlays can also provide significant environmental benefits. Sen et al. (2015) showed that the increased surface albedo of FFC inlays is capable of lowering surface temperatures to reduce heat island effects and global warming potential. Another promising benefit comes from incorporating titanium dioxide (TiO_2) nanoparticles into the cementitious matrix. As a semiconductor, TiO_2 is activated by UV-A radiation from sunlight, driving reactions with pollutants such as nitrogen

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oxides (NO_x) to remove them from the air (Devahasdin *et al.* 2003, Ballari *et al.* 2010). A schematic overview of the photocatalytic reaction with NO_x at a pavement surface is illustrated in Figure 1.

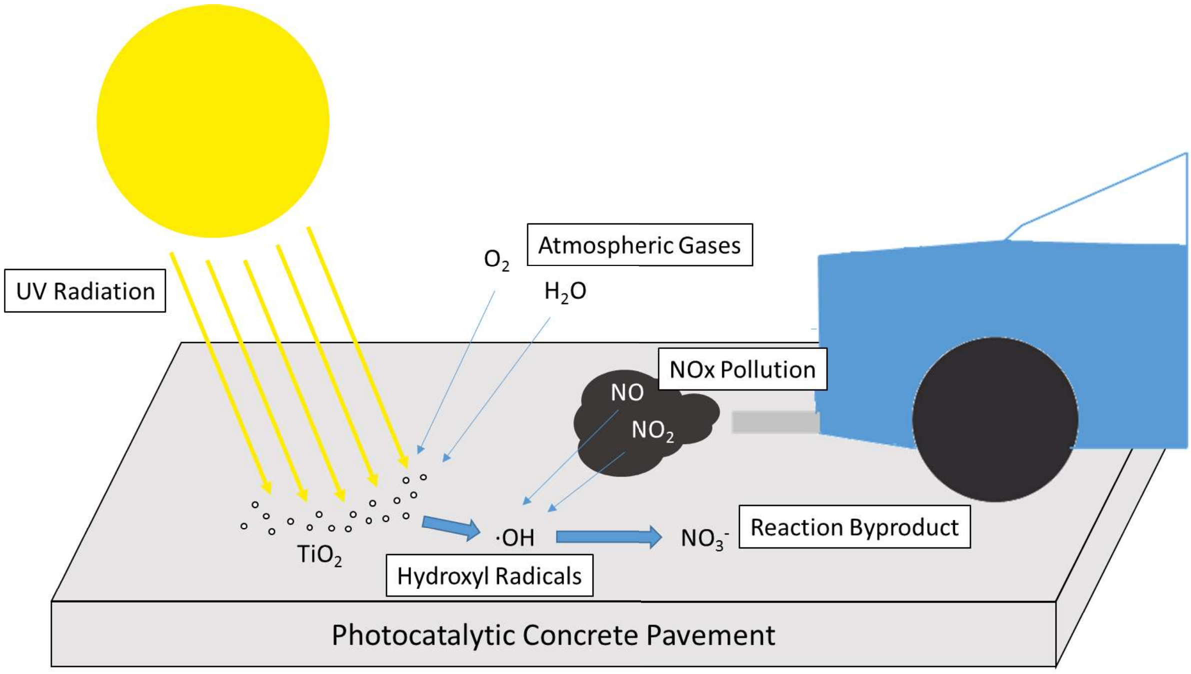

Figure 1. Overview of Photocatalytic Reaction at Pavement Surface.

NO_x, which consists of NO and NO_2, is one of the most prevalent air pollutants in urban areas. NO_2 concentrations in the near-road environment are regulated in the United States and worldwide because of their harm to human health and contribution to smog (Environmental Protection Agency 2010). Many researchers have demonstrated the NO_x removal ability of photocatalytic cementitious materials in the laboratory (Chen and Poon 2009, Ballari et al. 2010, Sikkema 2013, Lee et al. 2014, Jayapalan et al. 2015, Poon and Guo 2015) and their ability to react with NOx when incorporated into (or applied on top of) pavement surfaces and roadside structures (Guerrini and Peccati 2007, Cackler et al. 2012, Osborn et al. 2012, Terpeluk 2012, Boonen and Beeldens 2013). Sen et al. (2015) also verified the feasibility of incorporating TiO_2 nanoparticles into FFC mixes, showing that fresh and mechanical properties are preserved.

Currently, the overall effectiveness and best practices for promoting NO_x removal ability of photocatalytic concrete mixes have not been well defined. The primary goal of this study was to assess the effectiveness of photocatalytic FFC and to optimize the mix design for maximum NO_x removal capability. Photocatalytic mortar specimens were created with varying cement types and fly ash contents and evaluated in the laboratory to determine photocatalytic performance. Specimens were also artificially carbonated and then tested to quantify the effect of carbonation on photocatalytic efficiency and to investigate mitigation strategies. Spectrophotometer testing was also employed to determine the reflectance of each of the mix designs and to investigate the relationship between reflectance and photocatalytic ability. The results will assist in determining the effects of important variables such as mix design and carbonation and quantify the overall environmental benefits offered by thin, multi-functional FFC inlays.

Experimental Procedure

Test Specimen Preparation. Photocatalytic mortar specimens for NO_x removal and reflectance testing were prepared based on the FFC mix design developed by Bordelon and Roesler (2012) and later used by Sen et al. (2015), with a w/cm of 0.40. The specimens were made with a commercial photocatalytic cement (unknown TiO_2 addition rate), in which TiO_2 was pre-blended with Type I Portland cement. The specimens were mixed according to ASTM C305 (2014).

Mix designs were varied based on cement type and the addition of fly ash. Both white and gray TiO_2 cement blends were tested in this experiment to measure the impact of the surface reflectance on photocatalytic efficiency. Specimens containing each cement type were mixed alone (i.e. straight cement) or with 15% fly ash replacement. Fly ash was added to study the effects of carbonation, and samples for each mix design were subject to artificial carbonation. (Specimens with plain Type I cement containing no TiO_2 were also tested to verify that the nanoparticles were responsible for NOx removal.)

Laboratory testing of artificially carbonated photocatalytic mortar and paste samples has shown that carbonation is one of the most significant factors that can decrease the NOx removal ability of photocatalytic concrete (Chen and Poon 2009, Diamanti et al. 2013). Carbonation occurs when calcium hydroxide (CH), typically the second most prevalent hydration product, reacts with CO_2 in the atmosphere to precipitate $CaCO_3$. Chen and Poon (2009) proposed that the $CaCO_3$ byproduct reduced the porosity of the microstructure, allowing less UV-A radiation to reach TiO_2, while Diamanti et al. (2013) similarly theorized that the precipitated $CaCO_3$ shielded the TiO_2 nanoparticles from receiving UV radiation. Carbonation is mostly unavoidable in concrete exposed to the atmosphere because of the prevalence of CO_2. The addition of certain supplementary cementitious materials, including fly ash and silica fume, consumes some CH during hydration. For this study, fly ash was added to to investigate whether carbonation effects on the photocatalytic reaction could be reduced by decreasing the amount of CH available for reaction.

After three days of moist curing, the samples marked for artificial, accelerated carbonation were transferred to an incubator with a CO_2 content of 5% for 28 days, which is much higher than the atmospheric concentration of about 0.04%. Temperature was maintained at 22 ˚C, and RH was held between 55-80%. Carbonation of the sample surfaces was confirmed by treatment with phenolphthalein. Side-by-side images of the surface of non-carbonated and carbonated TiO_2 white specimens are shown in Figure 2. The uniform purple color of the specimen on the left demonstrates that the surface is still alkaline, indicating that carbonation has not occurred or was limited. Meanwhile, the absence of purple on the specimen on the right demonstrates that near-surface CH has been converted to $CaCO_3$ and the surface has been carbonated.

Figure 2. Side-by-side image of surfaces of non-carbonated (left) and carbonated (right) white TiO_2, 0% fly ash mortar specimens after treatment with phenolphthalein.

Photoreactor Testing. To measure NO_x removal ability of the mortar specimens, laboratory photoreactor testing was carried out according to ISO 22197-1 (2007), with some modifications to test conditions from Jayapalan et al. (2015). The specimen was placed in a plexiglass photoreactor chamber containing a borosilicate glass lid and illuminated by an overhead UV-A lamp. The irradiance reaching the specimen (10 W/m^2) was measured using a radiometer and controlled by adjusting the height of the lamp. A test gas consisting of NO and zero air was prepared for the experiment and regulated using mass flow controllers to achieve an inlet NO concentration of 500 ppb and relative humidity of 50%. A chemiluminescence analyzer measured the NO_x concentration at the outlet, after the test gas had passed through the photoreactor chamber and over the illuminated specimen. A diagram of the photocatalytic test setup is shown in Figure 3.

The main deviations from the ISO standard test conditions that were employed in this testing, based on the recommendations by Jayapalan et al. (2015), were to use an inlet NO concentration of 500 ppb (as opposed to 1000 ppb) and a test gas flow rate of 1 Lpm (as opposed to 3 Lpm). Although most testing of photocatalytic cementitious materials in the literature has also been performed according to ISO 22197-1, a wide variety of different testing conditions (e.g. NO concentration, UV irradiance, relative humidity) have been employed. Although the variety of testing conditions in the literature make it difficult to compare results, the conditions that were selected for this experiment were designed to make the test more representative of atmospheric conditions to which photocatalytic FFC inlays might be exposed and for ease of assessment of the relative performance of different mixes.

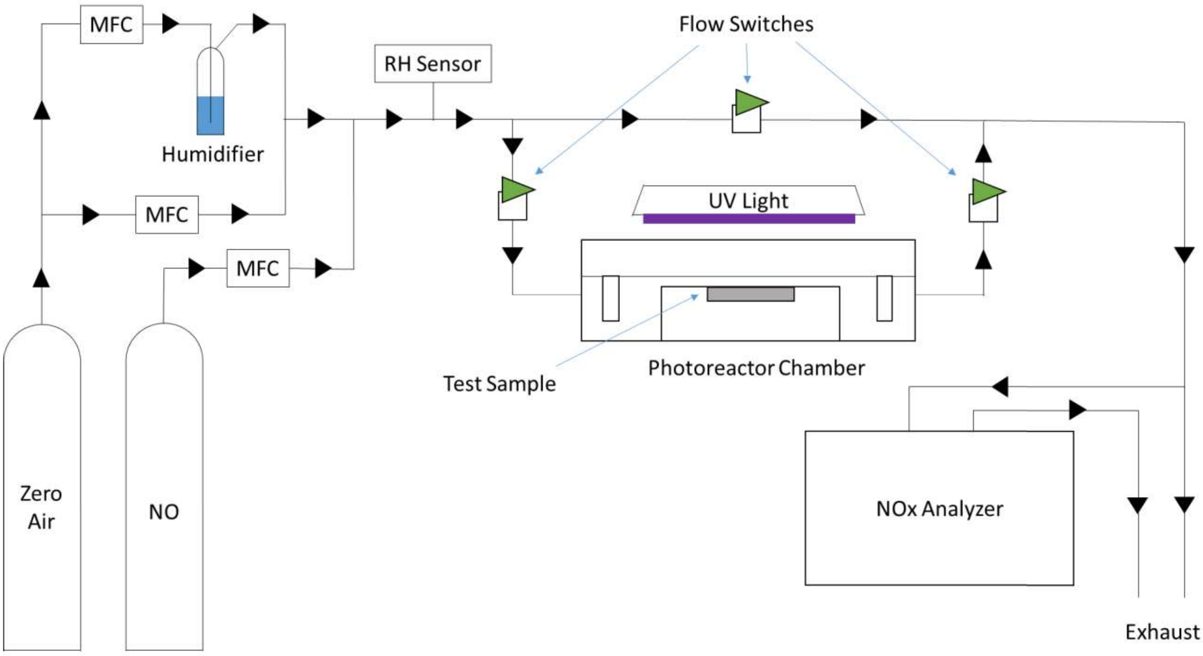

Figure 3. Photocatalytic Cement Test Setup. (MFC = Mass Flow Controller.)

The quantity of NO_x removed by the test sample during the experiment was characterized by the Photocatalytic Efficiency Factor, PEF (μmol/m^2·hr), a term introduced by Jayapalan et al. (2015). (Other researchers have also reported results using similar units (Chen and Poon 2009, Sikkema 2013, Lee et al. 2014, Poon and Guo 2015). PEF is defined according to Equation 1, where f is flow rate (Lpm), A is sample surface area (m^2), t is test time (hr), $[NOx]_{in}$ is the inlet NO_x concentration (ppm) measured in the first 30 minutes of the test before the UV lamp is turned on, and $[NOx]_{out}$ is the NOx concentration (ppm) measured after the gas stream reacts with the sample illuminated by UV light. To calculate PEF, $[NOx]_{out}$ concentrations were measured continuously with a 30 second averaging time and integrated over the total test time (5 hours).

$$PEF = \frac{f}{22.4 \times A \times t} \int_0^t ([NOx]_{in} - [NOx]_{out})dt \qquad 1$$

NOx removal efficiency of the reaction was also calculated according to Equation 2. The average $[NOx]_{out}$ across the entire test was subtracted from $[NOx]_{in}$ and expressed as a percentage of the inlet concentration.

$$NOx\ Removal\ Efficiency\ (\%) = 100\frac{[NOx]_{in} - [NOx]_{out}}{[NOx]_{in}} \qquad 2$$

Spectrophotometer Testing. Laboratory spectrophotometer testing was performed to characterize the average solar reflectance, or albedo, of the photocatalytic specimens. Sen et al. (2015) demonstrated that reflective photocatalytic concrete surfaces created with white cement can reduce heat island effects and global warming potential. However, in this experiment, reflectance was investigated to determine its relationship to photocatalytic performance. Previous work by Chen and Poon (2009) and Poon and Guo (2015) showed that photocatalytic cement paste specimens created with white cement were more photocatalytically active than those made with gray cement, and the authors suggested that it might be because of the increased reflectivity of the white cement specimens.

Albedo was measured for the photocatalytic mortar specimens using a Cary 5000 UV-Vis-NIR spectrophotometer according to ASTM E903 (2012). The range of wavelengths, λ, analyzed by the instrument was 280 nm to 2600 nm, covering UV, visible, and near-infrared radiation spectra. Calculation of albedo was carried out using the standard reference solar spectrum contained in ASTM G173 (2003). The spectrophotometer used while testing one of the white cement TiO_2 specimens is shown in Figure 4.

Figure 4. Testing of photocatalytic sample with UV-Vis-NIR Cary 5000 spectrophotometer.

Albedo values were calculated based on the reflectance across the entire range of wavelengths analyzed by the instrument, but reflectance in the UV-A spectrum was of particular interest since UV-A radiation is the catalyst of the photocatalytic reaction. Therefore, a separate metric, designated as UV-A reflectance, was also determined from the spectrophotometer data. UV-A reflectance was calculated in exactly the same fashion as albedo, but restricted only to values corresponding to the UV-A spectrum (315 nm ≤ λ ≤ 400 nm).

Results

Photocatalytic Performance. A typical photoreactor test result is shown in Figure 5, which plots the concentrations of NO, NO_2, and total NO_x over the course of the test. As seen in Figure 5, the inlet NO concentration was steady for the first 30 minutes of the test, i.e., inlet NO_x concentration matched the NO concentration, as there was no NO_2 in the test gas. At t = 30 minutes, the UV lamp was turned on, illuminating the test sample. Photocatalytic activity started immediately, marked by a large drop in NO concentration and the production of NO_2. A small concentration of NO_2 remained in the outlet stream, increasing slowly over the test time, but the majority of NO_2 generated during the test was also removed as NO_3^- by the photocatalytic sample, resulting in a large overall reduction in NO_x concentration (32.5%).

The result of the test plotted in Figure 5, with a steady increase in NO_2 concentration and a slight overall increase in NO_x concentration over the test time, was typical of most individual samples. In some instances, small decreases in NO_x concentrations were observed over time as well. After five hours of illumination, the UV light was turned off and NO_x concentrations returned to the inlet levels.

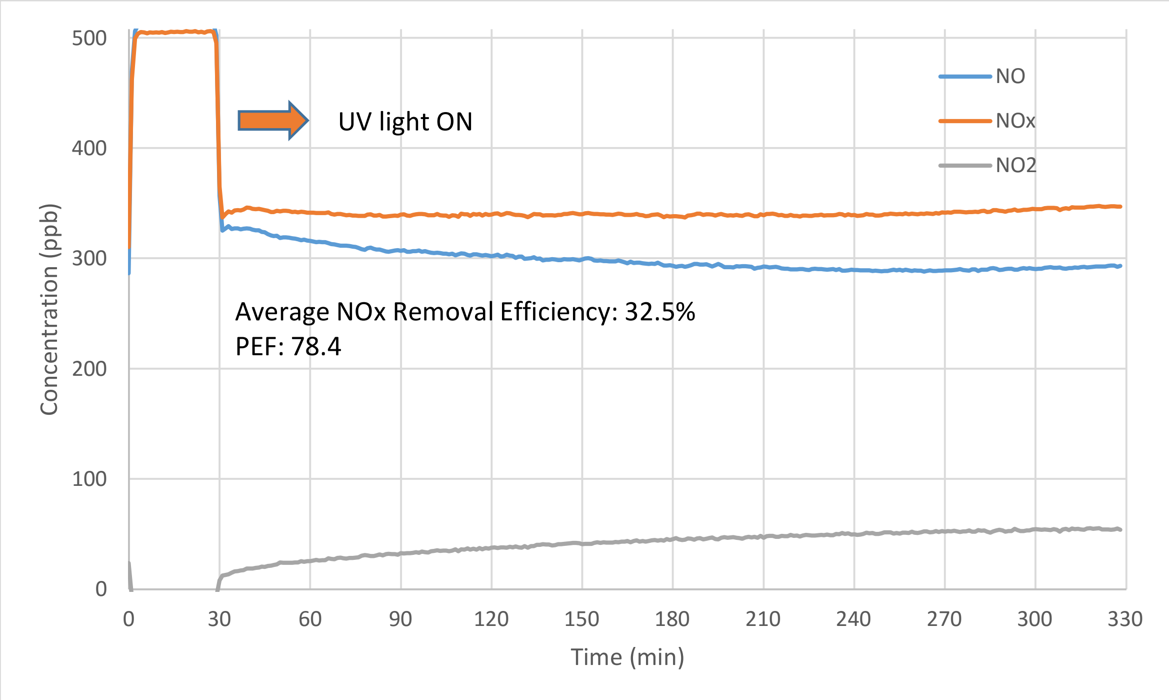

Figure 5. Typical photoreactor test result of photocatalytic mortar.

NO_x removal results for photoreactor testing are shown in Table 1, which provides the PEF and NO_x removal efficiency calculated for each specimen. The final column in Table 1 lists the decline in PEF found for each mix design because of carbonation. PEF and NO_x removal efficiency values for each mix were averaged from two specimens, except for TiO_2 gray, 0% fly ash, for which three specimens were tested.

Table 1: NO_x Removal Results for photocatalytic mortar samples.

Mix Design	Carbonation	PEF ($\mu mol/m^2 \cdot hr$)	NOx Removal (%)	PEF Decline due to Carbonation (%)
TiO_2 White, 0% Fly Ash	Non-Carbonated	112.3	48.1	75
	Carbonated	28.6	12.3	
TiO_2 White, 15% Fly Ash	Non-Carbonated	111.7	49.2	32
	Carbonated	76.5	33.0	
TiO_2 Gray, 0% Fly Ash	Non-Carbonated	45.1	19.4	65
	Carbonated	15.9	6.8	
TiO_2 Gray, 15% Fly Ash	Non-Carbonated	37.1	15.6	46
	Carbonated	20.0	8.3	
Plain Type I	Non-Carbonated	2.8	1.1	—
	Carbonated	-0.5	-0.2	

Albedo and UV-A Reflectance. A typical reflectance spectrum obtained from spectrophotometer testing is demonstrated in Figure 6. The spectral reflectance (total amount of monochromatic radiation reflected back from test sample surface as a percentage of incident monochromatic radiation) is plotted as a function of wavelength. The UV-A spectrum (315 nm ≤ λ ≤ 400 nm) is highlighted by a red box. The irradiance of the solar spectrum is also plotted in Figure 6 to indicate the relative weights of various parts of the spectrum used to calculate albedo. Albedo and UV-A reflectance results calculated from spectrophotometer testing are shown in Table 2. Values for each case are the average of measurements taken on two sides of single mortar specimens.

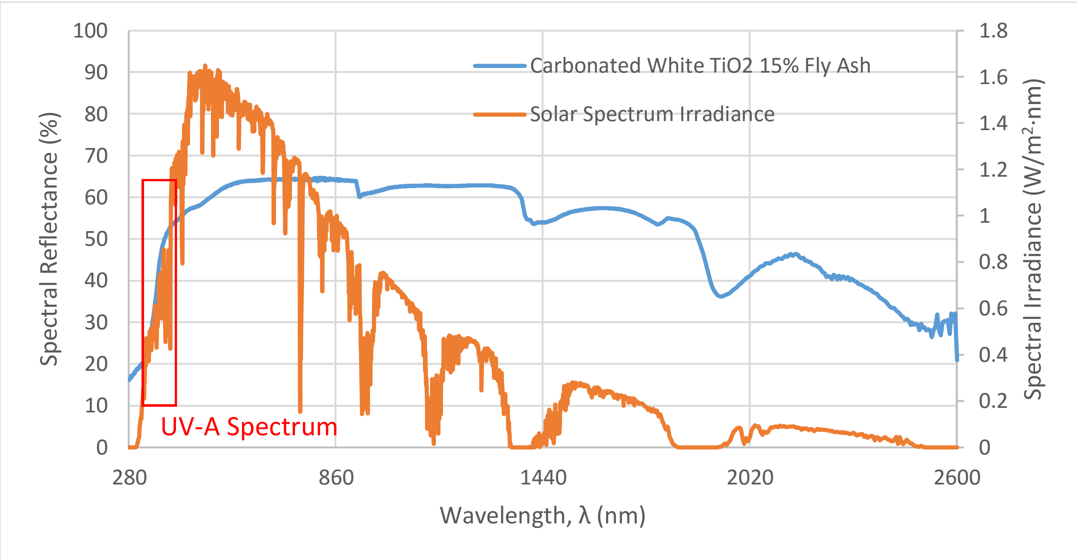

Figure 6. Typical reflectance spectrum with UV-A wavelengths highlighted in the red box.

Table 2: Albedo and UV-A Reflectance Results.

Mix Design	Carbonation	Albedo	UV-A Reflectance
TiO_2 White, 0% Fly Ash	Non-Carbonated	0.67	0.39
	Carbonated	0.62	0.37
TiO_2 White, 15% Fly Ash	Non-Carbonated	0.62	0.42
	Carbonated	0.56	0.34
TiO_2 Gray, 0% Fly Ash	Non-Carbonated	0.39	0.30
	Carbonated	0.30	0.19
TiO_2 Gray, 15% Fly Ash	Non-Carbonated	0.41	0.33
	Carbonated	0.36	0.25
Plain Type I	Non-Carbonated	0.37	0.32
	Carbonated	0.40	0.37

Discussion

Photocatalytic Performance. The photocatalytic performance of the mortar specimens in this experiment fell within the broad range of values that have been reported in the literature. Table 3 compares results from laboratory experiments that tested similar specimens to those in this study (in this case, TiO_2 with gray cement, 0% fly ash). As demonstrated in the table, a very wide range of results have been reported, resulting primarily from the sensitivity of the laboratory experiment to changes in test conditions.

Examining and comparing the test conditions of this experiment to those in the literature, it is possible to understand why the photocatalytic efficiency measured in this experiment differs from other tests and verify that these results are reasonable. For example, it is well-demonstrated (Ballari et al. 2010, Beeldens and Boonen 2012, Sikkema 2013) that testing at a lower relative humidity significantly enhances photocatalytic efficiency. Therefore, it makes sense that a test performed at 50% RH (such as in this experiment) would produce a lower PEF value than the tests performed at 30% RH listed in Table 3. Another major factor is inlet concentration. At a higher inlet concentration (e.g. 1000 ppb vs. 500 ppb), assuming the reaction proceeds at a similar efficiency, a greater amount of NO_x will be removed simply because there is a greater amount of NO_x present in the photoreactor system. Finally, curing also has a significant impact on photocatalytic performance (Chen and Poon 2009). With a longer curing time, photocatalytic performance is diminished. Therefore, a test in which the samples were cured at 28 days would not be expected to produce a PEF value as high as a sample tested at 3 days, such as in this experiment. Therefore, the PEF values obtained in this experiment appear to be reasonable relative to the literature and selected test parameters.

Table 3: Comparison to Results in Literature for Samples with Gray Cement.

Researcher	Photocatalytic Efficiency (μmol/m²·hr)	Testing Conditions
Current study	45.1	$[NO]_{in}$ = 500ppb, 50% RH, 1 Lpm, 10 W/m², 0.40 w/c, 3 day curing
Chen and Poon (2009)	80-130	$[NO]_{in}$ = 1000 ppb, 30% RH, 3 Lpm, 0.6 W/m², 0.35 w/c, 3-28 day curing
Poon and Guo (2015)	125	$[NO]_{in}$ = 1000 ppb, 30% RH, 3 Lpm, 2 W/m², 0.4 w/c, 1 day curing
Jayapalan et al. (2015)	8-22	$[NO]_{in}$ = 500 ppb, 50% RH, 1 Lpm, 10 W/m², 0.5 w/c, 14 day curing
Lee et al. (2014)	21.6-31.5	$[NO]_{in}$ = 1000 ppb, 50% RH, 0.5 Lpm, 10 W/m², 0.4-0.6 w/c, 28 day curing

Since photocatalytic efficiency is sensitive to changes in test conditions and results in the literature are variable, it can be difficult to assess the overall effectiveness of the photocatalytic mixes tested in this (or any) experiment and to project effectiveness in the field. On one hand, the NOx removal capability measured by laboratory testing in the current study and in the literature is an order of magnitude lower than the total NOx emissions by motor vehicles in the United States (Sikkema et al. 2013). On the other hand, much of these NOx emissions quickly dissipate into the atmosphere, leaving a lower but still-harmful concentration of NOx that lingers in urban areas and especially the near-road environment. In the context of near-road NOx concentrations, the values obtained in this experiment are promising.

Consider one study of a polluted near-road environment performed by Burkowicz (2000) at an urban street canyon in Berlin. Peak hourly NO_x concentrations at that site measured as high 300 ppb, which, depending on the ratio of NO to NO_2, would approach the US EPA limit for NO_2

of 100 ppb. This NO_x concentration corresponds to roughly 13 μmol/m^3 (depending on the assumed NO to NO_2 ratio). The most reactive, non-carbonated mix design tested in this experiment (white, 0% fly ash) demonstrated the ability to remove over 112 μmol of NOx per square meter of surface area per hour. Based on these results, a photocatalytic FFC pavement at the Berlin site would theoretically be able to react with all of the NOx present in a volume of air extending from the surface up to a height of nearly 9 m over each square meter of pavement surface. Even the least reactive, carbonated mix design tested in this experiment (gray, 15% fly ash) was able to remove nearly 16 μmol/m^2·hr of NOx in the laboratory, enough to theoretically remove all of the NOx present up to a height of over 1 m above the surface in one hour.

Field testing is required to fully understand the extent of the interaction between NO_x and the pavement surface in the near-road environment, accounting for factors such as wind and turbulence, and laboratory testing showed that the reaction does not proceed at 100% efficiency. Nevertheless, the results of this experiment are particularly promising because they were obtained at a more realistic relative humidity and were effective even after accelerated carbonation, demonstrating the potential impact of photocatalytic FFC inlays on the urban environment.

Effect of Surface Carbonation on Photocatalytic Performance. The results of the photoreactor testing showed that artificial carbonation led to a sharp decline in photocatalytic efficiency. The average decrease in PEF observed across all of the photocatalytic test samples was 55%. Notably, this decline was significantly worse than those previously observed in the laboratory by Chen and Poon (2009) and Diamanti *et al.* (2013), who measured decreases of roughly 30% and 25% in photocatalytic efficiency, respectively. These findings may have large implications on the viability of photocatalytic mix designs in which TiO_2 is mixed into the concrete mass, as carbonation is inevitable in the presence of atmospheric CO_2.

Fortunately, the addition of fly ash to the photocatalytic mix design somewhat mitigated the impact of carbonation to PEF. This effect was most clearly observed in the white TiO_2 specimens. As seen in Table 1, the mix containing 0% fly ash exhibited a 75% decline in PEF because of carbonation, while PEF for the 15% fly ash mix declined by just 32%. The decline caused by carbonation was also reduced from 65% to 46% by adding 15% fly ash to the gray TiO_2 specimens. With these samples, the fly ash in the mix was able to consume a portion of the CH, resulting in less carbonation of the sample surface and thus less interference with photocatalytic activity.

Effect of Albedo/UV-A Reflectance on Photocatalytic Efficiency. Samples made from white TiO_2 cement exhibited significantly greater NOx removal ability than the gray TiO_2 cement samples, and the primary difference between the white and gray TiO_2 mixes was reflectance. A scatter plot of PEF vs. UV-A reflectance for the non-carbonated samples is shown in Figure 7, which demonstrates the clear disparity in PEF between white TiO_2 and gray TiO_2. For the non-carbonated samples, UV-A reflectance of the white TiO_2 was about 30% higher than the gray TiO_2, and the correlation coefficient (r-value) between PEF and UV-A reflectance was 0.93.

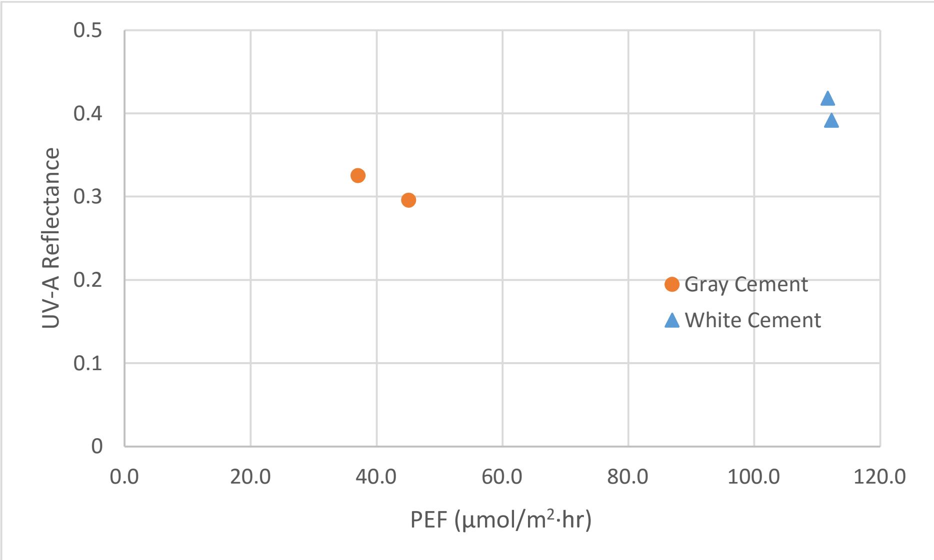

Figure 7. Relationship between UV-A reflectance and PEF for non-carbonated specimens.

The correlation between PEF and UV-A reflectance for carbonated specimens was reduced, with an r-value of 0.58. The weakening of this relationship in the carbonated specimens was likely a result of other changes to the mix that had competing effects on photocatalytic efficiency, primarily the addition of fly ash, which mitigated the effects of carbonation but also reduced overall TiO_2 content by replacing the photocatalytic cement. These factors also likely account for some variation in the PEF/reflectance relationship among non-carbonated samples. Overall, however, the correlation between UV-A reflectance and PEF was strong, identifying the reflectance of the concrete samples as one of the biggest factors in photocatalytic performance.

To explain why the reflectance of the mortar samples had such a large impact on photocatalytic efficiency, it is proposed to result from the phenomenon of diffuse reflection. Concrete (as well as mortar and paste), with its porous microstructure and rough surface finish, is an example of a diffuse surface (van Ginneken et al. 1998). Instead of reflecting back at the incident angle, light incident on diffuse surfaces is reflected with equal intensity in all directions in the half space around the surface (Siegel and Howell 2002). Figure 8 demonstrates the effect of diffuse reflection on the photocatalytic surface. Since the UV-A radiation is scattered in all directions, instead of just reflecting back out into the atmosphere, more radiation remains within the near-surface region through primary and secondary scattering and is able to reach TiO_2 sites that may have otherwise needed directly incident light to be activated. Therefore, the cumulative impact of diffuse reflection is to enhance photocatalytic activity, and the more reflective a photocatalytic surface is in the UV-A spectrum, the better it will be able to react with and remove NO_x from the environment.

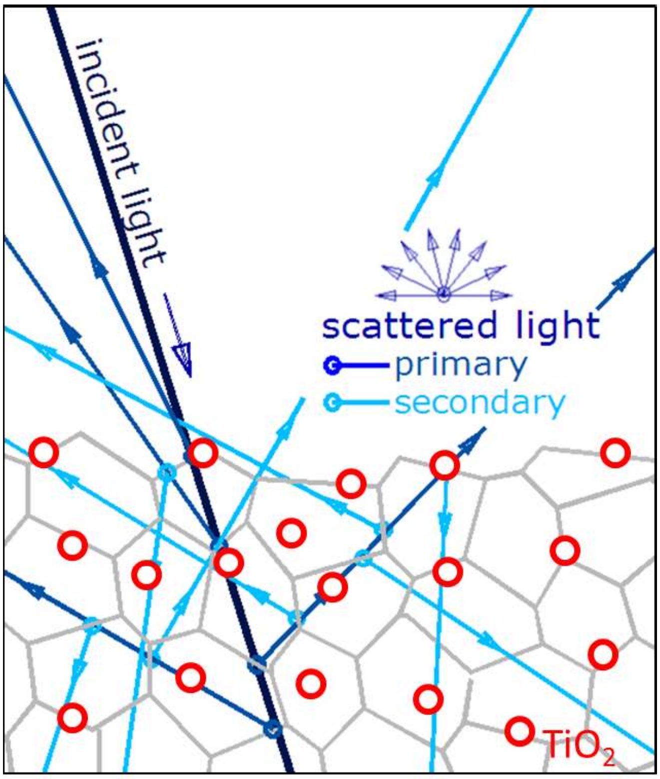

Figure 8. Demonstration of diffuse reflection at photocatalytic concrete surface (adapted from Wikipedia 2015).

UV-A radiation is the catalyst of the photocatalytic reaction between NO_x and TiO_2, so it is appropriate to focus primarily on the relationship between UV-A reflectance and photocatalytic performance. It should also be noted, however, that UV-A reflectance and albedo correlate very closely for all white and gray TiO_2 specimens (r-value of 0.99) and that the relationship between reflectance and photocatalytic efficiency is also strong if, instead of UV-A reflectance, albedo is considered instead (r-value of 0.98 for all non-carbonated specimens). While distinguishing albedo from UV-A reflectance may be trivial when analyzing data obtained from a spectrophotometer, albedo is easier to measure in the field and is a more common representation of reflectance in general. Therefore, it is valid and potentially more useful to point out that albedo correlates strongly with photocatalytic efficiency as well.

Conclusion

The potential environmental benefit of thin, multi-functional concrete inlays was determined through laboratory photoreactor testing and quantification of the NO_x removal ability of photocatalytic flowable fibrous concretes (FFC). Spectrophotometer testing analyzed spectral reflectance of FFC specimens and found white cement blended with TiO_2 nanoparticles offered enhanced photocatalytic efficiency compared to gray TiO_2 cement. Testing of artificially carbonated specimens revealed that carbonation had a substantially negative impact, cutting NO_x removal efficiency by an average of 54% and by as much as 75% for some mixes. Fortunately, the effects of carbonation were somewhat mitigated through the inclusion of fly ash in the mix.

Through quantifying the impact of different mix characteristics such as cement type and fly ash replacement on photocatalytic performance, the results of this study can be used to optimize an FFC (or any type of photocatalytic concrete) mix design for NO_x removal ability. Based on the mixes used in this investigation, a white TiO_2 cement concrete with 15% fly ash replacement would prove most effective by combining a high reflectance with resilience to carbonation. The NOx removal ability of this mix design, as well as each of the others considered in this study, demonstrated the potential to make a positive impact on the near-road urban environment and reduce the harmful impacts of NOx emissions.

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