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Quantification of NO_x reduction via nitrate accumulation on a TiO₂ photocatalytic concrete pavement

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QUANTIFICATION OF NO_x REDUCTION VIA NITRATE ACCUMULATION ON A
TiO₂ PHOTOCATALYTIC CONCRETE PAVEMENT

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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In

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by

David James Osborn
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ABSTRACT

Field trials of photocatalytic pavements were recently initiated and are presently being considered by many states (e.g., Virginia, Texas, New York, and Missouri). Results from this study originate from the country's first air-purifying asphalt and concrete photocatalytic pavements, constructed on Dec. 20, 2010. The test area is a pavement site located on the LSU campus. The objective of the study is to validate field photocatalytic degradation of NO_x in a field environment by measuring the day to day accumulation of the oxidized byproduct; nitrate salts (NO_3^-). The mass of nitrates, produced by the real life photocatalytic pavement, were measured. The measurement was then correlated to the same mass of nitrates as recovered from laboratory samples with recorded NO_x reductions in accordance to the Japanese Industrial Standards. This paper presents a nitrate sampling procedure, to be administered in the field, without the need for core sampling. Based on the results of the experimental program, the proposed method, quantify photocatalytic efficiency through nitrate measurements, was successful. There is evidence that photocatalytic degradation of nitrogen oxide was occurring in the treated section when compared to the control. The photocatalytic process was highly active during the first four days, followed by a decrease in the degradation rate of NO_x . The decreased degradation activity might be caused by a continuous decrease in ambient NO_x levels that occurred during the collection. Full regeneration of photocatalytic activity occurs in the field through a self-cleaning process during a rain event. Six months of traffic and in-service operating conditions proved to have negligible effects on the durability of the photocatalytic coating, when comparing the mass of nitrates recovered to just after installation. In addition, there was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation with the laboratory experiment at the same level of relative humidity.

CHAPTER 1

INTRODUCTION

United States, as a nation, faces major challenges in controlling air pollution resulting from transportation activities and the growing population density. Certain regions in the US were designated by the US EPA as nonattainment areas in which air pollution levels persistently exceed National Ambient Air Quality Standards (NAAQS). The critical pollutants for attainment are inclusive of carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), ozone (O₃), lead (Pb), and particulate matter (P.M.) [EPA 2010]. Louisiana is situated in a non-attainment area for 8 hour ozone in major Parishes like East and West Baton Rouge, Ascension, Iberville, and Livingston [EPA 2011]. Although attempts are continuously made to lower vehicle emission standards, a method is needed to remove these pollutants once they are emitted to the atmosphere. This is particularly important in urban and metropolitan areas, where tall buildings prevent the dispersion of air pollutants from road traffic, and where the origin is at street level.

Due to its capacity to oxidize NO_x pollutants when illuminated by ultra violet (UV) light, titanium dioxide (TiO₂) has the potential to play a significant role in pollutant abatement. Recent laboratory-scale studies have demonstrated that incorporation of TiO₂ surface coatings on to construction material surfaces may reduce concentrations of gas-phase NO_x and SO₂, two critical air pollutants emitted by motor vehicles [Mueller and Nowack 2008; Dylla et al. 2010; Hassan et al. 2010; Dylla et al. 2011]. This approach holds great promise for mitigating air pollution problems, particularly in population-dense urban areas.

While application of TiO₂ surface coatings may be effective in reducing the environmental impacts of vehicle air emissions, none of the research conducted to date were able to validate the benefits of this technology in the field or to formulate theoretical models that can predict the rate of NO_x degradation based on field and environmental conditions. Therefore, validation of the effectiveness of photocatalytic pavements under field climatic and operational conditions carries the potential to expand use of this sustainable technology to mitigate many problems associated with pollution from motor vehicles.

1.1 PROBLEM STATEMENT

Despite the aforementioned advantages, current applications of photocatalytic technology are limited to building facades and gateway elements of bridges not subjected to traffic as in the case of the I-35W Bridge over the Mississippi River in downtown Minneapolis. In addition, this new technology has not been tested in Louisiana. This may be attributed to a lack of research results quantifying its effectiveness under field, climatic, and operation conditions. In the field, measuring the pollution reduction of NO_x in relation to photocatalytic pavements often presents a challenge, due to the large influence of various parameters, time, and costs. A critical need exists to simplify the field measurement efficiency of photocatalytic pavements by adopting indirect techniques to measure NO_x degradation. For example, indirect techniques may be used to measure the photocatalytic degradation of NO_x by measuring the nitrate (NO_3^-) deposited on the surface as it is a direct product of the decomposition of NO_x .

The results of this research will be of significant value to practitioners and researchers. Field trials of photocatalytic pavements either were recently initiated or presently are being considered by many states (e.g., Virginia, Texas, New York, and Missouri). For instance, the Missouri Department of Transportation (MDOT) is currently preparing for a trial section of photocatalytic pavement in the St. Louis area. Yet these test sections are constructed without a clear quantification of the benefits of photocatalytic pavements in the field and without knowledge of the durability or the long-term effectiveness of the coating.

1.2 RESEARCH OBJECTIVES

To address the aforementioned shortcomings, the ultimate goal of this study was to validate NO_x degradation due to photocatalytic activity by measuring accumulating byproduct, NO_3^- , on a TiO_2 , spay-coated, concrete pavement. To achieve this objective, the study made use of a newly constructed demonstration site on LSU campus. Through this study, the following objectives were achieved:

- Quantify the concentration of nitrate deposited on the pavement surface using the EPA-

approved colorimetric method (cadmium reduction) and UV Vis Spectrophotometer.

- Develop a method to extract the nitrates from the pavement surface.
- Compare the results of field effectiveness of photocatalytic pavement to laboratory effectiveness under controlled environmental and operational conditions.
- Predict field NO_x reduction efficiency based on sound theoretical concepts.

1.3 RESEARCH APPROACH

To achieve the aforementioned objectives, the conducted research activities were divided into five main tasks. First, field samples were collected by dissolving the nitrates deposited on the pavement surface in Deionized (DI) water. Second, the concentration of nitrate was quantified in the laboratory using the cadmium reduction method and UV Vis Spectrophotometry. The measured nitrate concentrations were then used to backcalculate NO_x reduction efficiency using Stoichiometry. Finally, results of the field effectiveness of photocatalytic pavements were compared to results of the laboratory effectiveness measured under controlled conditions, with a recorded NO_x reduction. To this end, the following research tasks were conducted:

Task 1: Develop a method to extract the nitrates from the pavement surface

The objective of Task 1 was to develop a method to extract the nitrate ions (NO_3^-) deposited on the concrete photocatalytic pavement surface as a result of photocatalytic reaction. This method controls: (1) surface area; (2) quantity of DI water; and (3) time of surface washing to ensure that the collected samples are comparable to each other. Therefore, a custom made wooden collection device was used as shown in Figure 1.1.



Figure 1.1 Wooden collection device with plumber's putty

As shown in Figure 1.1, the device is composed of a 2" X 8" X 18" untreated piece of wood. A 4" X 6" rectangle was removed from the center. In the opening, 40 ml of DI water is placed left for 5 minutes, and then recollected using a luer lock syringe with a 0.45µm filter attached. Plumbers putty was placed around the perimeter of the opening in the device and weight was applied on top to ensure a good seal and prevent loss of the DI water due to horizontal water flow. A stopwatch was used to measure the five minutes needed for soaking.

Task 2: Collect nitrate field samples

The objective of Task 2 is to measure photocatalytic activity by quantifying the daily accumulation of nitrates on a photocatalytic pavement surface for 7 consecutive days. Photocatalytic activity can be detected by comparing the level of nitrates collected from the photocatalytic surface to the level of nitrates collected from the control area. For the seven days collection, seven locations were marked on the pavement. The seven locations were adjacent to one another, forming a 1 X 7 column. To account for error and variability, three samples were collected each day, thus forming three columns of seven as shown in Table 1.1. The pavement surface was washed thoroughly with 10 gallons of water on day zero. Then, the nitrate samples were collected using the method described in Task 1. The nitrate concentration obtained from the samples collected in day zero, immediately after the wash, served as a baseline for the nitrate analysis. At the close of 24 hours after the wash, day 1, the aforementioned method in Task 1 was used to collect locations A1, B1 and C1 from both the photocatalytic area and the control area. The samples were then transported to the lab for immediate analysis. 24 hours after the day 1 collection, locations A2, B2 and C2 were collected from both the photocatalytic area and the control area, and so the procedure was established.

Table 1.1 Example of the treated and untreated collection areas.

Location-Day		
A-1	B-1	C-1
A-2	B-2	C-2
A-3	B-3	C-3
A-4	B-4	C-4
A-5	B-5	C-5
A-6	B-6	C-6
A-7	B-7	C-7

Task 3: Conduct the experimental program to quantify the concentration of nitrate in the collected field samples

The objective of this Task 3 was to quantify the concentration of nitrates in the collected water samples. The process used UV Vis spectroscopy in conjunction with colorimetric methods in order to measure the concentration of dissolved nitrates in an aqueous solution. By this method, cadmium metal reduces nitrates to nitrites. The nitrites react by means of an acidic medium with sulfanilic acid to form an intermediate diazonium salt. In turn, the salt reacts with chromotropic acid to form a pink-colored solution. The intensity of color in the solution is proportional to the concentration of nitrate in the sample. The light absorption measured using UV VIS spectroscopy then is correlated to nitrate concentration by means of a standard calibration curve. Test results are measured at 507nm.

Task 4: Compare the results in the field and in the laboratory

The objective of Task 4 is to measure and compare NO_x reduction efficiency of concrete photocatalytic pavements in the field as well as in a controlled laboratory where the

environmental conditions may be replicated. To achieve this task, concrete samples with photocatalytic surfaces similar to the pavement surface in the field were tested in the laboratory using a novel setup shown in Figure 1.2. The laboratory test setup was modified from the Japanese Industrial Standard (JIS) TR Z 0018 “Photocatalytic materials – air purification test procedure”. The laboratory setup permits various operational and climatic conditions, in this task, the humidity varied at three different levels 30%, 50%, and 80%. The remaining conditions were kept constant. Nitrates were collected from the lab samples after each test run. Results were compared with field collected nitrates after a one day accumulation.



Figure 1.2 Illustration of the Experimental Laboratory Setup

Task 5: Analyze collected and laboratory data to quantify NO_x reduction

The objective of this Task 5 is to quantify the field NO_x reduction efficiency, based on the concentration of nitrates recovered from the field. Stoichiometry back calculation can convert a concentration of nitrate (mg/L) to a mass of nitrogen (g) to concentration of NO (ppmV). The relative humidity, witnessed in the field, may be compared to the results for the same relative humidity in the laboratory samples, and thus efficiency can be predicted. Therefore, a) when the relative humidity in the field matches the relative humidity in the lab experiment, and b) the

concentration of nitrates removed from each are similar, it may be assumed that the efficiency observed in the field is similar to the efficiency observed in the lab. The following steps were used to convert nitrate to nitrogen oxide:

Step 1: Convert nitrate concentration from mg/l to mole of NO/l knowing the molecular weight of NO_3^- and NO;

Step 2: Convert NO concentration from mol NO/l to mass of contaminants in g NO/l;

Step 3: Determine volume of NO contaminant in liter based on the ideal gas law as follows:

$$V_{\text{contaminant}} [\text{L}] = \frac{\text{Mass}_{\text{contaminant}} [\text{g}]}{\text{Molecular Weight}_{\text{contaminant}} \left[\frac{\text{g}}{\text{mol}} \right]} \times 8.3144 \left[\frac{\text{L.kPa}}{\text{mol.K}} \right] \times T_{\text{air}} \times \frac{1}{P_{\text{air}} [\text{kPa}]} \quad (3)$$

where,

$V_{\text{contaminant}}$ = volume of NO contaminant in liter;

$\text{Mass}_{\text{contaminant}}$ = determined from Step 2; and

T_{air} and P_{air} = temperature and pressure of air.

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CHAPTER 2

LITERATURE REVIEW

2.1 HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis was discovered by Fujishima and Honda in the 1970's. Fujishima was researching photo-electrochemical solar energy conversion when the study shifted to environmental photocatalysis including photo-induced hydrophilicity. Heterogeneous photocatalysis is a process involving a catalyst that absorbs UV energy from the sun and oxidizes organic matters in either the atmosphere or aquatic environments. Hydrophilicity is a process involving self-cleaning by water to dissolve the molecular entity of any surface contaminant. Although the photochemistry between photocatalysis and hydrophilicity are completely different, both can occur simultaneously, as with titanium dioxide (TiO₂) semiconductor particles [Fujishima 2000].

Although the potential of titanium dioxide as a photocatalyst was discovered by Fujishima and Honda in 1972 [Fujihima 1972; Hassan et al. 2011], it was not until the mid-1990's that the technology was used for air purification. This process shown in Figure 2.1, which is similar to plant photosynthesis, allows a decomposition of water into oxygen and hydrogen in the presence of light, by means of a TiO₂-anode in a photochemical cell according to the following reaction [Fujishima 2006; Hassan 2010]:



A semiconductors' photocatalytic ability is dependent on the amount of energy in the semiconductors band gap. The most commonly used semiconductors are SrTiO₃, TiO₂, ZnO, ZnS and CdS. TiO₂ has the greatest amount of energy in the band gap consisting of 3.23 eV [Zhao and Yang 2003]. When semiconductors are exposed to UV energy that is equal to or surpasses the amount of energy in the semiconductors band gap, an electron from the valence band is expelled to the conducting band. When this occurs, an oxidizing hole is created that is used for breaking water molecules (H₂O) into hydroxyl radicals (OH) and superoxides (O₂). These components are then used in the degradation of pollutants. One of the unique features

of this process is that it does not depend on the intensity of the light and just a few photons generated from an ordinary room light can be sufficient to initiate the photocatalysis reaction [Jacoby et. al. 1996].

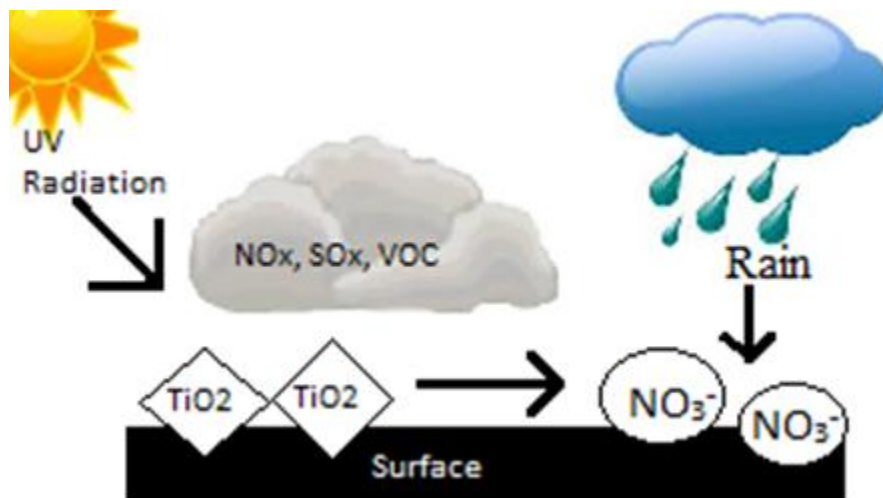


Figure 2.1 Mechanism of Photocatalysis

For environmental purification, it is desirable to prepare a titanium dioxide coating with super-hydrophobic properties, which provide for a self-cleaning surface. Through this process, particles of contaminants adhere to water droplets in the event of rain and are removed from the surface when the droplets roll off the surface. The following sections identify the climatic and operating conditions that affect photocatalytic efficiency.

2.1.1 Types of Titanium Dioxide

For a semiconductor such as TiO₂, photocatalytic efficiency is dependent on the size, shape, type, and modifications of the semiconductor particles. Titanium dioxide particles crystallize in three forms: anatase, rutile, and brookite. Anatase is a meta-stable phase that transforms into rutile at high temperatures [Znaidi et al. 2001; Hassan et al. 2011]. The anatase phase is the most powerful photocatalyst semiconductor in environmental purification [Bilmes et al. 2000; Dylla 2011]. It is the anatase crystalline modification that controls the photocatalytic efficiency of TiO₂ [Husken et al. 2009]. However, the predominantly used TiO₂ coating currently is in the

rutile form due to its abundance and low cost [Bendix et al. 2000]. Nano-sized TiO_2 in range of 6-15nm present a large surface area, which enhances photocatalytic degradation efficiency. The crystalline shapes vary with the manufacturing process and therefore are different for each manufacturer.

2.1.2 Photodegradation Capabilities

Research identifies three main pollutants that can be degraded in the presence of titanium dioxide photocatalyst: nitrous oxides (NO_x), sulfur oxides (SO_x), and volatile organic compounds (VOCs). NO_x is identified by EPA as a critical pollutant, and contributes to smog, acid rain, ground level ozone, and sick building syndrome. Researchers have reported photocatalytic degradation efficiencies of NO_x to be over 80% in the laboratory [Dylla et al. 2011]. The oxidation of nitrogen oxide by means of this photocatalyst process is described as follows [Fujishima et. al. 2000]:



Sulfur oxides (SO_x) are also a contributor to smog, and acid rain that results in building degradation and reduction of biodiversity in terrestrial and aquatic regions [Dylla 2011; Poon and Cheung 2007]. The two focused VOCs are BTEX and formaldehyde. BTEX; benzene, toluene, ethylbenzene and o-xylene are the most common indoor VOC pollutants. Studies show that the removal efficiency of toluene and o-xylene have reached over 90% [Ao et al. 2004]. Formaldehyde is a VOC that causes cancer. Ao et. al. (2004) conducted research on how SO_x , NO_x and BTEX interacted when degraded simultaneously. It was observed that formaldehyde degradation was enhanced in the presence of NO, but decreased in the presence of SO_2 [Ao et al. 2004]. Researchers are continually attempting to better understand degradation rates of TiO_2 on different pollutants through the study of the pollutants chemical kinetics [Dylla 2011].

2.1.3 UV Intensity

The energy provided by UV light is necessary for heterogeneous photocatalysis to occur. Without UV light, photocatalytic oxidation does not occur as reported by several researchers [Anpo and Takeuchi 2003; Zhao and Yang 2003; Nonami et al. 2004; Dylla 2011; Poon and Cheung 2007; Liu et al. 2008]. Varying levels of UV intensity often have a linear relation to degradation rates where higher intensities produce more photons and associate with higher degradation rates [Fujishima et al. 2000; Zhao and Yang 2003; Dylla 2011]. However this correlation is dependent on the chemical pollutant. A study on the oxidation activity of the four VOCs; BTEX, revealed that when irradiance was increased from 0 to 1500 $\mu\text{W}/\text{cm}^2$, the degradation rates were linear, yet changed drastically for o-xylene and ethylbenzene and only slightly for benzene and toluene [Strini et al. 2005]. Another study revealed that the photocatalytic degradation of Trichloroethylene (TCE) increased from 0.08×10^{-6} to 0.25×10^{-6} mol/s g in relation to the light intensity changing from .08mw/cm² to 0.45 mw/cm² [Zhao and Yang 2003].

2.1.4 Relative Humidity

Research indicates that the levels of humidity have a direct effect on photocatalytic efficiency. Although water remains a key component to the oxidation of pollutants, due to its necessity for the formation of active hydroxyl radicals and superhydroxides, excessive water vapor reduces photocatalytic efficiency [Zhao and Yang 2003; Wang et al. 2007; Demeestere et al. 2008; Sleiman et al. 2009; Hassan et. al. 2010]. The reason for the reduced efficiency in the presence of high concentrations of water vapor is not entirely clear. One explanation may be that as the relative humidity increases, layers of water accumulate on the surface and prevent the pollutant from contacting TiO_2 [Sleiman et al. 2009]. Another suggestion is that water vapor and pollutants may compete for the adsorption sites [Wang et al. 2007; Demeestere et al. 2008; Sleiman et al. 2009; Dylla et. al. 2010]. An ideal relative humidity ranges from 20% to 40% in case of photodegradation of NO_x [Hassan et al. 2012].

The effect of relative humidity also varies with the type of pollutant being tested. For example, Sleiman observed no optimal relative humidity for the photocatalytic performance on toluene [Sleiman et al. 2009]. On the other hand, Zhao and Yang experienced only decreasing efficiency with increased humidity [Zhao and Yang 2003]. The study of the effect of humidity on formaldehyde photocatalytic degradation resulted in two different outcomes. Ao et al. (2004) observed that when the humidity was increased from 2100ppmv to 22000ppmv, photocatalytic efficiency decreased from 80% to 54% [Ao et al. 2004]. However, Liu et al. reported an optimum relative humidity of 55% [Liu et al. 2008]. Hassan and co-workers conducted a detailed evaluation of the effects of relative humidity (RH) on the efficiency of titanium dioxide on concrete pavements. The study prepared photocatalytic samples in the laboratory by varying TiO₂ content between 3% and 5%, and by varying the aggregate gradation with and without fines. Three levels of relative humidity were observed, 30%, 50%, and 80%. Results indicated that for the 30%, 50% and 80% RH, NO_x was reduced by approximately 40%, 22.5% and 12.5%, respectively [Dylla et al. 2010].

2.1.5 Flow Rate and Pollutant Concentration

Research studies varied flow rates between 1 L/min and 9 L/min to provide information on the effect of flow rate on photocatalytic degradation efficiency [Yu 2003; Beelden 2006; Dylla 2011; Chen and Li 2007; Poon and Cheung 2007]. Results showed that increased flow rates reduce residence time and in effect reduce degradation rates, conversely decreased flow rates increase the amount of contact time between the pollutant and the photocatalytic surface resulting in a more efficient photocatalytic oxidation [Ao et al. 2002; Demeestere et al. 2008; Sleiman et al. 2009]. For example when flow rates of toluene were increased from 70 ml/min to 350 ml/min, the photodegradation of toluene decreased from 95% to 65% [Sleiman et al. 2009].

Higher pollutant concentrations increase the competition and accumulation of the adsorption sites and thereby reduce efficiency, while decreased pollutant concentrations result in an increase of photocatalytic efficiency [Ao et al. 2002; Demeestere et al. 2008; Sleiman et al. 2009]. For increased efficiency when combining concentration with flow rates, lower

concentrations and lower flow rates present a positive impact on photocatalytic degradation as shown in studies of VOC degradation by TiO_2 [Ao et al. 2002; Zhao and Yang 2003; Demeestere et al. 2008; Sleiman et al. 2009].

2.1.6 Regeneration and Degeneration of TiO_2

Research shows that over time the photocatalytic efficiency of titanium dioxide (TiO_2) decreases (degenerates) with continuous use. Nevertheless, the efficiency can be regenerated by a wash using water or rain. The catalyst itself is stable in the environment and theoretically can be used indefinitely [Nonami et al. 2004; Dylla 2011]. The loss of efficiency may be attributed to the fact that the photocatalytic surface becomes covered by the accumulation of oxidized pollutants, dirt, oil, etc. [Zhao and Yang 2003; Yu 2003]. In this case, a regenerative method is required to remove these products to restore photocatalytic efficiency [Nonami et al. 2004; Dylla 2011]. Another reason may be a loss of titanium dioxide particles due to wear or abrasion.

Martinez et al. (2011) studied the degradation rates from photocatalysis oxidation on two different substrates, glass and mortar. Results showed that glass substrate degenerates at a faster rate compared to mortar. Moreover, the NO_2 generation was more prevalent with the glass substrate due to the lack of adsorption capacity on glass as well as the competition of NO with NO_2 for oxidation [Martinez et al. 2011].

Maximum regeneration has been observed with rain simulation or water soaks. Beeldens (2008) used this practice in a field study on photocatalytic pavement blocks. The blocks were extracted from the field and brought to the lab for testing. An ability for photocatalytic NO_x oxidation was observed prior and post surface washing. Results indicated that washing played a significant role in the regeneration of photocatalytic capability [Dylla 2011; Beeldens 2008; Hunger et al. 2008].

2.2 PHOTOCATALYTIC DEGRADATION OF NO_x

The mechanism described in Equations (2) and (3) through which TiO_2 accelerates the decomposition of air pollutants such as NO_x from air in the presence of UV light is shown in

Figure 2.1. Studies conducted to identify the effect of substrate on NO_x degradation via heterogeneous photocatalysis suggest that titanium dioxide films are greatly affected by the substrate material [Ma et al. 2000]. Results indicate that NO_x degradation effectiveness is dependent on the absorption capacity of the substrate.

Martinez studied the impacts of three different substrates on NO_x degradation efficiency with 1) mortars, 2) glass, and 3) nonabsorbent cardboard. Results showed that the mortar substrate exhibited constant degradation efficiency throughout a five hour experiment, while the glass substrate did not. The glass substrates' initial efficiency was similar to that of mortar, but over time, the displayed efficiency decreased [Martinez et al. 2011]. That result was attributed the fact that the nitrate initially converted was first deposited on the surface. Since glass has low absorption, the deposited nitrate ions occupying the adsorptive site also prevented NO_x particles from coming into contact with the TiO₂ film. However, the NO reduction efficiency on the glass substrate displayed a slight degradation rate decrease [Ma et al. 2000; Martinez et al. 2011].

Other substrate characteristics were found to have effects on photocatalytic activity as well. In the study performed by Yu and Zhao (2003), sodium and calcium diffusion from the borosilicate glass substrate had detrimental effects on photocatalytic activity. As a result, concrete pavements are considered the ideal substrate due to a high adsorption capacity, combined with a necessity to be as close as possible to the source of pollution [Beeldens 2008].

2.3 USE OF TITANIUM DIOXIDE IN CONSTRUCTION APPLICATIONS

Researchers recognize the air purification potential of TiO₂ for urban and metropolitan areas that suffer high air pollution concentrations [Benedix 2000; Poon 2007; Hassan et al. 2011]. A number of research studies have suggested the use of a thin film application of powdered TiO₂ as a coating to a number of substrates [Poon 2007]. The number of titanium dioxide patents are continually growing and currently include materials in concrete tiles, concrete paving, and white cement (architectural concrete), on building surfaces, as well as applying environmentally-friendly cement (TioCem) [Sopyan 1996; Yoshihiki 2002; Heidelberg 2008].

Despite recent advancements in heterogeneous photocatalysis, current applications of this technology are limited to building facades and sculptures, and are usually employed more for self-cleaning rather than air purification. As a result, the photocatalytic coatings for buildings are not subjected to those traffic loads common to highway pavements. In addition, application of titanium dioxide becomes an added cost. Currently, thin films are considered to be the most efficient method of application for photodegradation since the titanium dioxide becomes concentrated on the surface. However, under environmental conditions, the possibility of delamination poses a concern that delamination might limit the durability of the layer. Therefore, a durable heterogeneous photocatalytic concrete surface layer must be designed to withstand traffic loads of highway pavements while effectively utilizing the photocatalytic abilities of TiO_2 .

2.3.1 Application Methods

Titanium dioxide technologies are mostly directed towards concrete applications in which a fine mixture consisting of cement, sand, TiO_2 , and water is applied as a thin surface layer or slurry to the pavement surface. To achieve the necessary mechanical strength for the surface layer, a minimum mixture of cement to aggregate ratio of 1:3 has been recommended for the use in the surface layer [Poon and Cheung 2007]. However, this minimum ratio reduces the NO removal rate by as much as 30%. An alternative method of application is to use photocatalytic concrete paving blocks with a thin layer of TiO_2 coating [Beeldens 2008]. This may prove attractive in terms of manufacturing and installation; however, it may not be cost-effective due to the large volumes of air that must be processed, thus rendering the practical implementation of this technology an uncertain choice [Beeldens 2008]. Alternative methods of applying TiO_2 to concrete pavements include spraying TiO_2 nanoparticle suspended in a binding agent or sprinkling TiO_2 nanoparticles on curing concrete [Chen et al. 2007; Hassan et al. 2010]. Photocatalytic overlays are preferred amongst researchers due to their durability [Dylla 2011; Beeldens 2008; Diamanti et al. 2008]. Nonetheless, the spray coating application has an advantage of being more easily constructed and potentially cheaper in applications to existing pavements.

2.3.2 Application of TiO₂ to Pavements

Evaluation of concrete pavements treated with titanium dioxide provided promising results as recent research shows that a thin surface coating is able to remove a significant portion of NO_x, SO_x, and VOC pollutants from the atmosphere when placed as close as possible to the source of pollution [Beeldens 2006; Dylla 2011; Hassan 2010]. It was reported that each square meter of titanium dioxide coating, subject to sunlight, can remove nitrogen oxides and VOCs from about 200m³ and 60m³ of air per day, respectively [Berdahl and Akbari 2008]. The efficiency of this technology depends on the size of the surface exposed, the concentration of pollutants, the humidity, and the ambient temperature. Porosity of the surface is also important as the NO_x removal ability is improved as the porosity is increased. Photocatalytic activity decreased by approximately 8% with aging of the surface but stabilized at the age of 90 days [Poon and Cheng 2007]. The deposition of pollutants on the surface was reported to decrease efficiency of removal but it can be regained through the self-cleaning mechanism [Beeldens 2008].

Research results by Hassan and co-workers in recent years have measured the impact of common roadway contaminants including motor oil, dirt, and de-icing salt on the effectiveness of photocatalytic roadways' ability to remove NO_x from the atmosphere [Dylla et al. 2011]. Results of the experimental program showed that the three contaminant types had a strong negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminants' coverage was largely dependent on the soil type with oil having the largest negative impact. An increase in the flow rate and air relative humidity also resulted in lower NO_x efficiencies. Hassan and co-workers also evaluated the environmental effectiveness of a TiO₂ coating to photo-degrade mixed NO₂ and NO gases from the atmosphere [Dylla et al. 2011]. Results of the experimental program determined that an increase in the flow rate and NO₂/NO_x ratio negatively affects the effectiveness of the photocatalytic process. However, the extent of this impact depends on many other factors including flow rate.

A few studies attempted to use TiO₂ in asphalt pavements [Li and Qian 2009; Venturini and Bacchi 2009]. In Italy, TiO₂ was incorporated into asphalt pavements as a thin surface layer

to be sprayed on existing pavements [Venturini and Bacchi 2009]. The water-based emulsion was applied by two different methods (hot and cold) distinguished by the spraying of the emulsion either during asphalt pavement laying operations when the pavement temperature is over 100°C, or on existing pavements at ambient temperatures [Venturini and Bacchi 2009]. The study results showed that reduction efficiencies were highly dependent on the type of TiO₂ nanoparticles used with NO_x reduction, with efficiency ranging from 20 to 57%. Meanwhile, researchers in China mixed TiO₂ with an asphalt binder, applying 2.5% content of the binder weight to an emulsified asphalt pavement [Li and Qian 2009]. This study achieved a maximum efficiency in removing nitrogen oxide near 40%. A more efficient approach may be achieved by concentrating the photocatalytic compound at the pavement surface.

2.3.3 Photocatalytic Field Studies

To date, the field evaluation of photocatalytic pavement technology has been limited. A recent study in Italy attempted to apply the photocatalytic compound as part of a water-based emulsion [Guerrini and Peccati 2007]. Beeldens (2008) researched an 8mm thick, wearing layer, with titanium dioxide applied to the surface of existing pavement blocks. This thickness was selected so that when the surface was subjected to abrasion, TiO₂ would still be present on the surface [Beeldens 2008].

The Nanjing No.3 Bridge over the Yangtze River was spray coated with TiO₂. One end of the bridge was spray coated while the bridge was being cast and cured. When the bridge opened, NO_x levels were recorded at the north and south ends of the bridge. Nitrogen oxide concentrations on the bridge were collected from both ends of the bridge; the non-coated end was considerably higher than the photocatalytic end [Li and Qian 2009]. Another study quantified NO_x degradation in a pilot street using TiO₂ mortar panels. This study measured photocatalytic efficiencies under field environmental conditions and controlled pollution levels. TiO₂ was mixed in mortar and the walls of the street canyon were treated. A reference wall was left untreated. Results confirmed that the NO_x levels were significantly higher on the reference wall when compared to the TiO₂ treated wall [Maggos et al. 2007].

Additional field studies presently are being considered by many states (e.g., Virginia, Texas, Vermont, New York, and Missouri). For instance, the Missouri Department of Transportation is currently constructing a trial section of photocatalytic pavement in the St. Louis area [Portland Cement Association 2010].

2.4 MEASUREMENT OF PHOTOCATALYTIC EFFICIENCY IN THE LABORATORY

NO_x removal photocatalytic efficiency can be measured in the laboratory under controlled conditions in accordance to a standardized method for testing photocatalytic surfaces that has been established by the Japanese Industrial Standards (JIS); JIS R 01701:2004 (Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for air purification performance of photocatalytic materials – Part 1: Removal of nitric oxide). The experimental setup consists of a pollutant source, zero air source, calibrator, humidifier, photoreactor, and a chemiluminescent NO_x analyzer as shown in Figure 2.2. The setup simulates different environmental conditions by allowing for control of light intensity and air humidity. The pollutants are introduced through an inlet jet stream to a photocatalytic testing device, “the photoreactor”. A zero air generator is used to supply the air stream, which is passed through a humidifier to simulate the desired humidity level. Fluorescent lamps, attached to the photocatalytic device, are used to imitate natural sunlight radiation required for photocatalytic activity (Hassan et. al. 2012).

The pollutants measured from the recovered air before and after the photocatalytic device allow for a determination of the absorbed level of pollutants. Nitrogen-oxide removal efficiency was measured using the Thermo Chemiluminescent NO_x analyzer [JIS 2004]. The Thermo 146i Gas calibrator was used to supply a defined concentration of gas for the experimental setup at a controlled flow rate. Nitrogen oxide (NO) subsequently is blown over the surface at a constant concentration and flow rate. Testing is conducted for a total time of five hours; however, the photocatalytic process initiates after 30 minutes from the beginning of the test in order to ensure that steady concentration is reached in the environmental chamber [Hassan et. al. 2012].

After the sample is tested as specified by JIS R 01701: 2004, nitrates are to be removed from the sample. To remove the nitrates, the sample is immersed in a known quantity of water

for one hour. After one hour, the sample should be immersed in a second known quantity of water for another hour. The sample is then removed and the weight for both quantities of remaining water is recorded. The two remaining bodies of water need to be analyzed for nitrate ion concentration, according to JIS K 0101. One method for determining nitrate concentrations is by the use of colorimetric method cadmium reduction. This method could be used for field verification as well [Beeldens 2008].

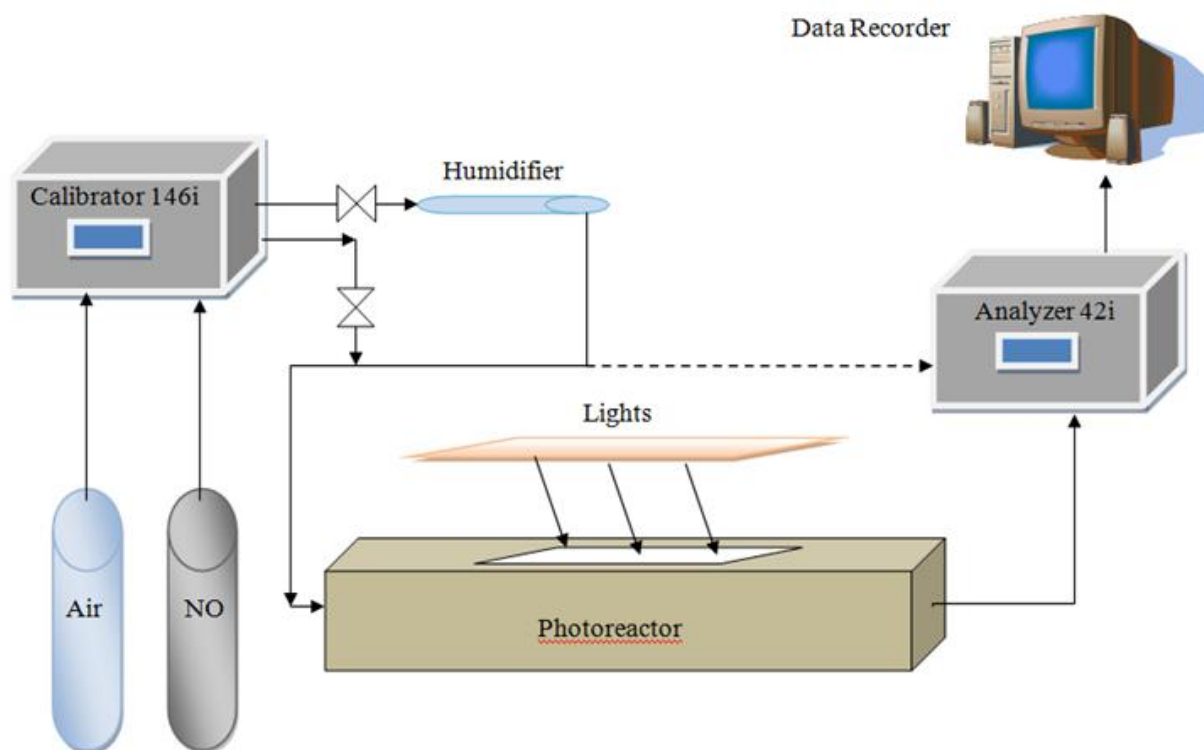


Figure 2.2 Mechanism of Laboratory NO_x Analysis

2.5 MEASUREMENT OF PHOTOCATALYTIC FIELD EFFICIENCY

Continuous measurement of NO_x photocatalytic degradation in the field often presents a challenge because of the numerous influencing parameters, as well as time, and costs [Dylla et al. 2012]. Despite the application of multiple photocatalytic field studies, some researchers concluded that none of the current field studies had demonstrated a determinate NO_x reduction resulting from photocatalytic pavements [Hunger 2010]. Nevertheless, photocatalytic field studies are considered to be the next step in advancing this technology. To date, projects

utilized two methods to measure photocatalytic degradation from field studies, both the direct and the indirect method. The direct method involves quantifying the reduction by measuring the ambient air pollution concentration at pavement level while the indirect method measures the byproducts created from the degradation process i.e., the nitrates deposited on the pavement surface [Dylla et al. 2012].

Nitrogen oxides are considered the most commonly used pollutant to quantify the efficiency of photocatalytic pavements. It is easy to monitor nitrogen oxides emitted from vehicle combustion in the air as well as to measure the photocatalytic byproduct of the reaction, nitrates ions. In addition, roadway microenvironments contribute 58% of NO_x emissions, causing detrimental environmental effects by promoting acid rain in the outdoors, and by contributing to sick building syndrome and other indoor air quality challenges [Kuhns et al. 2004].

Chemiluminescence is used for direct NO_x reduction measurements from photocatalytic pavements. Chemiluminescence occurs when light is emitted from a reaction between NO and ozone. The quantity of light emitted is proportional to the NO concentration [Dylla et al. 2012]. For nitrogen dioxide (NO_2) quantification, an indirect method is used. A catalytic converter is first used to reduce the nitrogen dioxide to nitric oxide. The NO measured after the catalytic conversion is added to the initial measurement of NO and the combined measurements of NO and NO_2 correspond to NO_x concentration. Therefore, NO_2 concentration is the difference between the two measurements, one measurement is recorded before the catalytic convertor and the other is recorded afterward [EPA 1999; EPA 2007; Dylla et al. 2012]. Another method of testing NO_x concentrations is to use a filter to trap the gaseous pollutants and then analyze the filters, using colorimetric methods to determine concentrations [Chen and Chu 2011; Dylla et al. 2012].

A majority of the field studies have used the chemiluminescent technique to monitor NO_x concentrations of ambient air subjected to photocatalytic treatments, as well as ambient air outside the photocatalytic area; the difference between the two is considered to be the

degradation provided by photocatalysis. This method is capable of comparing the two areas under similar environmental conditions. One field experiment adopted this method, applying a chemiluminescent method to measure the NO_x reduction for 1 hour each month. The process recorded a NO_x reduction as high as 80% in the photocatalytic pavement, compared to the untreated area [Li and Qian 2009]. Meanwhile, field studies that use traps have witnessed reductions up to 16% [Chen and Chu 2011; Dylla et al. 2012]. However, to better understand the photodegradation activity involved with photocatalytic pavements, continuous monitoring under various environmental conditions is necessary. Environmental conditions impact photodegradation efficiency, as well as parameters such as wind, that influence pollutant dispersion, even in relatively small distances [Maggos 2008].

Due to the implications associated with the transfer from laboratory to field studies, intermediate steps were explored in the form of pilot studies. A pilot study controls as many parameters as possible while allowing environmental variables to take effect. In France, a pilot study was conducted to evaluate the photodegradation rates associated with TiO_2 treated street canyon walls. Controlled parameters included pollution source and distribution, while variables included environmental conditions. Two measurements were conducted on the canyon walls. The first measured a wall panel that had been treated with TiO_2 photocatalytic mortar. The second was an untreated reference wall panel. The pilot study suggested that a difference in NO_x pollution observed from the two measurements was the photodegradation efficiency from the photocatalysis [Maggos et. al. 2008; Dylla et. al. 2012]. Results revealed that NO_x reduction efficiency was observed between the levels of 36% and 82% depending on pollution concentration, as well as wind strength and direction [Maggos et. al. 2008; Dylla et al. 2012].

The second technique adopted in this study involves the use of indirect measurements to quantify photocatalytic reductions. NO_3^- is a direct result of oxidized NO_x and thus is deposited on the photocatalytic surface that initiated its oxidation. An indirect measurement of NO_x photodegradation would be to quantify NO_3^- accumulation on the photocatalytic surface. The collection of nitrates becomes feasible due to its solubility in water; therefore, if water could be used to wash the surface and then recollected, the water could be analyzed for nitrate

concentrations [Beeldens 2008]. The quantification of NO_3^- collected from the photocatalytic surface may be used to indirectly calculate, using the stoichiometry given in Equations (1) and (2) to determine the amount of photodegradation of NO_x [Beeldens 2008]. Beeldens used an indirect technique of measuring nitrate concentrations; the researcher suggested that 2 mm NO_x/m^2 can be removed in 12 hours [Beeldens 2008]. However, field results could not relate photocatalytic reduction efficiency to impacting factors such as traffic, wind, light, humidity because some nitrates were not eluted and were left on the surface [Beeldens 2008; Beeldens 2011].

2.6 NITRATE COLLECTION METHODS

Methods for nitrate sampling by use of water are diverse but require a few necessary components. The container that stores the sample for transportation from the collection site to the laboratory should be sterile and composed of either glass or polyethylene. After collection, the sample should be kept in a dark environment at or below 4°C [EPA 2011]. There are many different collection methods. Selection of a collection method should be based on the end result or purposes. For instance, point source sampling, such as rivers or pipelines, should collect water from the middle of the stream [EPA 2011]. In case of nonpoint sources, collection devices such as the Coshocton-Type Runoff Sampler and the Gerlach Trough Runoff Sampler can be used, shown in Figures 2.3 and 2.4. Automatic samplers continuously collect during a rain event with intervals based on time or the flow rate of water. The site of the sampler should be located downstream from high water turbulence where the sediment variation is minimized. The area of water being collected may then be determined using a hydrograph. Volume of each sample is predetermined [Pathak 1991].



Figure 2.3 Coshocton-Type Runoff Sampler, Adopted from [Rickly 1997]



Figure 2.4 Gerlach Trough Runoff Sampler, Adopted from [Rickly 1997]

2.7 NITRATE DETECTION METHODS

There are many methods approved for the quantification of nitrates in aqueous solution. Three of the most commonly used methods are discussed: a) Ion Chromatography (IC), b) the colorimetric method of cadmium reduction coped with an electronic spectrophotometer, and c) nitrate electrode. IC uses ion-exchange resins to determine accurate estimates of nitrate content in the water; the determination is based on interactions with the resin [Everett et al. 1995]. The EPA recommends the use of IC in the determination of inorganic anions in water samples [EPA 1993].

The cadmium reduction is a two-step process that begins by bringing the nitrates in contact with the cadmium to reduce all nitrates to nitrite. Then, the nitrites react with another reagent to form a pinkish color. The intensity of the pinkish color is proportional to the amount of nitrate, which can be accurately measured with the use of UV Vis spectroscopy. The UV Vis provides absorption counts proportional to the intensity of the color. The absorption counts can then be used to find the concentration of nitrates when related to a standard calibration [EPA 2010].

A nitrate electrode consists of a sensor on the end of a probe, capable of measuring nitrate activity in water. In the probe is a solution with an electrical potential that changes due to nitrate activity. Any change in electrical potential is transmitted to a meter where the change is converted to a scale read in millivolts. The instrument correlates the millivolts to the concentration of nitrates by means of a standard calibration [EPA 2010].

2.8 HAZARDOUS ENVIRONMENTAL RISKS AND IMPACTS OF PHOTOCATALYTIC PAVEMENTS

Preliminary risk assessments of the technology identified two main risk categories: environmental impacts of both intermediate and end products of the technology, and nano particle exposure. The following sections discuss the main risks of photocatalytic pavements.

2.8.1 Potential Environmental Impacts of Photocatalytic Pavements By-Products

Photocatalytic oxidation is capable of degrading NO_x , SO_x and VOCs as discussed above. Additional benefits include reduction in ground level ozone, smog, and acid rain [Cassar 2005; Hassan 2010]. Potential environmental impacts of the technology include eutrophication due to nitrate formation, acidification due to sulfate formation, and nano exposure [Lippiatt 2002]. In addition, the photodegradation of five main VOCs was studied to identify the intermediate products, formaldehyde and BTEX (benzene, toluene, ethylbenzene, and o-xylenes). The intermediate product from formaldehyde is formic acid [Yang et al. 2000; Ao et al. 2004]. Formic acid is used as a pesticide in honey bee hives; however, it is toxic in the human body and causes metabolic acidosis [Rowe and McCollister 1981]. The intermediates of toluene were benzene, benzaldehyde and benzoic acid [Ao et al. 2004; Sun et al. 2010]. Health impacts for benzaldehyde are slightly hazardous on the skin, but very hazardous in case of ingestion. Benzoic acid is used in some medicines and is also a food preservative; however, in large doses, it can be toxic. Data from these studies may be used to quantify impacts on the environment and human health.

Ground level ozone usually occurs during the summer season and is caused by NO_x and VOC emissions, when combined with sunlight and heat. Ground level ozone is usually prevalent in urban areas, due to large quantities of NO_x and VOC pollutants combined with the heat island

effect, which is typical of the urban climate, yet ground level ozone also occurs in rural locations. Human effects of ground-level ozone include a) irritation to the respiratory system, b) reduced lung function, c) aggravate asthma, d) inflammation and damage to the lung lining, e) a reduction in immune system responses. A common environmental effect of ground-level ozone is smog [EPA 2012]. Acid rain occurs when sulfur dioxide and nitrogen oxide react with water, oxygen, and other chemicals in the atmosphere. Acid rain directly impacts the environment by causing acidification of lakes and streams, damaging trees and soil, and decaying buildings and statues [EPA 2007]. Therefore, with lower concentrations of NO_x , SO_x and VOCs in the atmosphere, these many harmful effects would be reduced. However, by-products of the photocatalysis of these pollutants include nitrates, sulfates and intermediates of VOCs; the effects of these by-products must be evaluated.

2.8.2 Nano Exposure Risks

Engineered nanoparticles (ENPs) are currently rapidly growing in the environment. ENPs have found their way into textiles, electronics, pharmaceuticals, cosmetic and environmental remediation [The Royal Society and The Royal Academy of Engineering 2004; Dunphy Guzman et al. 2006]. The technology proposed in this study utilizes engineered nano TiO_2 in the form of photocatalytic pavements. This section discusses some of the potential risks associated in ENPs.

Two competing suggestions have been made regarding the widespread use of nanoparticles. Optimists suggest nanotechnology can reverse environmental impacts that have been imposed since the industrial revolution [Navarro et al. 2008]. Yet it is undisputable that as the production increases, ENPs will intrude into aquatic, terrestrial, and atmospheric ecosystems [Nowack and Bucheli 2007] the long term impact of that intrusion is not entirely understood [Navarro et al. 2008]. For instance, most plants, algae and fungi have cell walls that act as a primary defense to the penetration of ENPs. However, some species, such as diatom algae, are uniquely composed of semipermeable cell walls that allow the passage of particles smaller than 20nm [Fujino and Itoh 1998; Fleischer et al. 1999; Zemke-White et al. 2000;

Madigan et al. 2003; Navarro et al. 2008]. With an increase in particle permeability, reproduction may change the pore size of diatom algae [Wessels 1993; Ovecka et al. 2005; Navarro et al. 2008]. As nano particles pass through the cell walls, a cavity is formed, further pulling the particles into the cell. When this occurs, the interference with the metabolic process as well as the nucleus of the macrophage, may result in degeneration, enlargement, and rarefaction [Jia et al. 2005; Navarro et al. 2008].

Furthermore, plants with higher leaf area indexes are at risk of ENPs in the atmosphere due to the ENPs entrance into the trophic webs. Forests with large surface area combined with large amounts of evapotranspiration could act as efficient traps to ENPs. When ENPs accumulate on the leaf surfaces, there might be the possibility of penetration of the trichomes or stoma that subsequently could move to other tissues. As the ENPs on a leaf surface become abundant, foliar heating and alteration of gas exchange may occur. In aquatic systems, the toxicity of ENPs may directly affect algae productivity. In addition, indirect effects may include ENPs attaching to forms of algae, thereby resulting in sunlight blockage to the algae cells or an increase in cellular weight that could result in cell sinking [Huang et al. 2005; Navarro et al. 2008].

ENPs may also affect the protection of phytopathogens and oxidative stress fungi that in turn provide for plants [Hildebrandt et al. 2007; Navarro et al. 2008]. Some ENPs could be consumed by bacteria and thus be introduced to food webs [Kloepfer et al. 2003; Hardman 2006; Navarro et al. 2008]. Once inside the food web, the ENPs could transfer to larger animals, where the acidic conditions of the animals' digestive system might change the particle aggregation. However, due to major unanswered questions concerning ENP effects on the environment, such as a concentration of ENPs, exposure routes, mechanisms for ENP passage through cellular walls, properties related to toxicity, and ENP trophic behaviors, transfers effects are not confirmed and may be unrealistic [Navarro et al. 2008].

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CHAPTER 3

QUANTIFICATION OF NO_x REDUCTION VIA NITRATE ACCUMULATION ON A TiO₂ PHOTOCATALYTIC CONCRETE PAVEMENT¹

3.1 INTRODUCTION

Self-cleaning, air-purifying pavement is a rapidly emerging technology that can be constructed using air-cleaning agents with photocatalytic capabilities such as Titanium Dioxide (TiO₂). Photocatalytic compounds applied to the pavement surface have the benefits to be in close contact with vehicle emissions as well as the advantage of being naturally more effective during times when pollutants tend to be higher (i.e., during daylight). This technology is especially promising for city roads where trends of urban development and increase in traffic volumes add to emissions while street canyon conditions inhibit their dispersion resulting in high ground level pollutant concentrations. Recent research has shown that a thin TiO₂ surface coating is able to remove a significant portion of Nitrogen Oxides (NO_x) pollutants from the atmosphere when placed as close as possible to the source of pollution (1).

Because of its capacity to catalyze oxidative reactions when illuminated by UV light, TiO₂ has the potential to play a significant beneficial role in pollutant abatement. Recent laboratory-scale studies from researchers throughout the world have demonstrated that incorporation of TiO₂ surface coating on to construction material surfaces can reduce concentrations of gas-phase NO_x emitted by motor vehicles (1-4). While application of TiO₂ surface coatings may be effective in reducing the environmental impacts of vehicle air emissions, limited research conducted to date was able to validate the benefits of this technology in the field or to relate laboratory measurements of NO_x reduction efficiency to field efficiency.

Given the potential environmental benefits of TiO₂, field trials of photocatalytic pavements were recently initiated and are being considered by many states (e.g., Virginia, Texas, New York, and Missouri). For instance, the Missouri Department of Transportation

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(MDOT) is currently preparing for a trial section of photocatalytic pavement in the St. Louis area. However, a clear quantification of the benefits of photocatalytic pavements has not been established in the field. Hassan and co-workers laid the country's first air-purifying asphalt and concrete photocatalytic pavements on Dec. 20, 2010 (5). The test area is a pavement site located on LSU campus. The objective of this study is to validate field photocatalytic degradation of NO_x on the test site by measuring nitrate salts (NO₃⁻) deposited on the pavement surface. A field sampling procedure of nitrate salts deposited on the pavement surface is presented. By quantifying the nitrate levels produced in the field due to photocatalytic activity, measurements were correlated to laboratory test results of NO_x reduction efficiency.

3.2 BACKGROUND

Several methods have been suggested to reduce vehicle emissions such as lean NO_x traps and Selective Catalytic Reduction (SCR). However, drawbacks exist with both techniques such as potential of producing secondary pollutants and thermal durability. An alternative solution is heterogeneous photocatalysis in which a semiconductor activated by light at a particular wavelength creates hydroxyl radicals, (*OH) and superoxides (O₂⁻) that accelerate the natural decomposition process of organic and inorganic pollutants (6). In contrast to other methods, pollutants are decomposed with little energy requirements and little selectivity (7). In addition, their super-hydrophilic properties allow them to self-clean in the presence of rain (8). A proposed mode of oxidation of nitrogen oxides via hydroxyl radical intermediates in the presence of photocatalysis is as follows, Figure 3.1 (8):



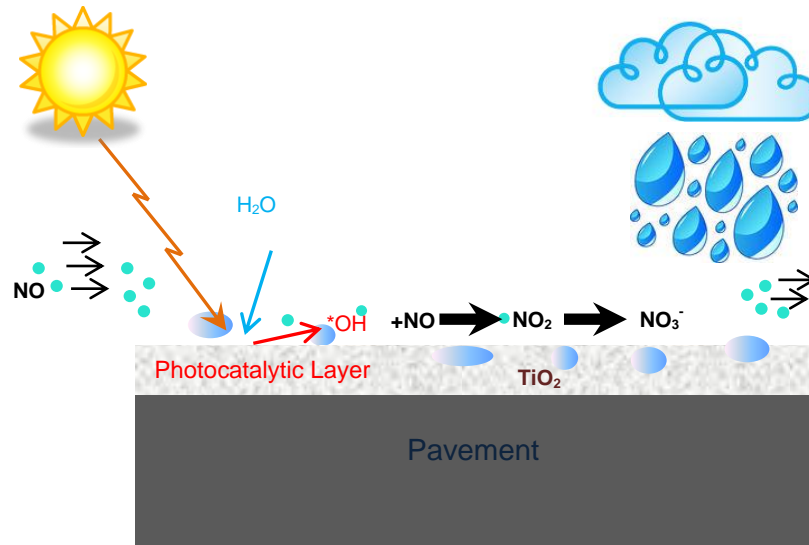


Figure 3.1 Illustration of the Photocatalytic Process

Various studies have incorporated photocatalytic oxidation in building materials for NO_x reduction. Beelden (2008) studied photocatalytic concrete blocks' ability to decompose NO_x pollutants. The concrete blocks consisted of an upper cement coat containing TiO_2 (9). Poon and Cheung (2007) incorporated TiO_2 into several different concrete surface mix designs by changing the aggregates design (10). Hassan et al. (2010) evaluated three methods of application for TiO_2 to concrete pavement, a cementitious-based ultra-thin coating, a water-based titanium dioxide solution, and sprinkling TiO_2 to the fresh concrete surface before hardening (2). The environmental benefits of applying an ultra-thin TiO_2 coating or a water-based TiO_2 solution were greater than the sprinkling method.

Although photocatalytic oxidation was proven effective in reducing NO_x emissions in the laboratory, field evaluation of photocatalytic pavement technology has been limited. To measure the pollution reduction of NO_x continuously in the field often presents a challenge, due to a large number of influencing parameters, time, and costs. As a result, researchers have attempted to simplify field tests by adopting indirect techniques to measure photocatalytic degradation and by controlling some of the variables. For example, indirect techniques can be used to measure the photocatalytic degradation of NO_x by measuring the nitrate (NO_3^-) deposited on the surface as it is a direct product of the decomposition of NO_x , see Equations (1)

and (2). Nitrates, water-soluble, are washed from the surface with water and can be measured using ion chromatography and other laboratory test methods (8).

3.3 EXPERIMENTAL PROGRAM

3.3.1 Field Test Site

Hassan and co-workers laid the country's first air-purifying photocatalytic asphalt and concrete pavements on Dec. 20, 2010. The test area is a pavement site located on LSU campus, Figure 3.2. A customized distributor truck was used in the application of TiO_2 water-based solution. Two parameters were necessary to remain constant during the application: speed and pressure. To maintain an accurate and steady speed of 50 ft per minute, a magnet was placed on the drive shaft that counted each revolution. The distance covered per revolution was calibrated by counting the number of rotations, as the truck drove 100 ft. Knowing the revolutions per minute and the distance per revolution, the speed was calculated and digitally displayed to the driver in order to maintain a constant speed. With the speed constant, the pressure was adjusted such that a surface layer of 1 ml/sf was applied. Mounted on the back of the truck, a spray bar fitted with nozzles distributed the TiO_2 water-based solution. To ensure full coverage, the nozzles were spaced accordingly in order to coat the entire width of the road with at least 1 ml/sf. A surface coat of 1ml/sf creates a slightly damp appearance not visible in Figure 3.2. Thus, the visible streaks seen in Figure 3.2 are areas with excessive coating. Additional methods of application may need to be developed to optimize material use. The spray coating used was a mixture of TiO_2 anatase nanoparticles with an average size of 6nm suspended in an aqueous liquid at 2% by volume.



Figure 3.2 Field Application of Photocatalytic Pavement Coating

3.3.2 Nitrate Field Sampling

Since nitrate salt is a direct product of photocatalytic activity, field measurements were conducted to quantify the amount nitrate deposited on the pavement surface, Equation (2). The nitrate salts deposited on the pavement were measured for seven consecutive calendar days for the treated section and a nearby untreated section, six months after application. Since water was used to dissolve nitrate salts at the pavement surface, a new sampling location, adjacent to one another to form a large square with 3 columns and four rows, was used each day as repetitive applications of water to a single location would clean the surface and may introduce a source of errors in the measurements. In each collection day, three different samples, from the coated and uncoated locations, were taken and the average was calculated to account for variability. Therefore, a total of 42 sampling locations (three per day on the treated section and three on the untreated section repeated for seven days) were used. These sampling locations were selected outside shaded, cracked, and depressed areas and were marked on the pavement surface. Heavy rain storms were also avoided such that the seven days collection period was completely dry. These measurements were correlated to laboratory measurements to estimate the levels of NO_x removed from the ambient air via TiO_2 photocatalysis.

A preliminary light wash was administered on the selected locations to remove any existing nitrates from the pavement surface. A nitrate baseline collection cycle was conducted on both the treated and untreated sampling locations. To collect the deposited nitrate, a custom-made nitrate collection device was manufactured. The device consisted of an untreated wood piece with a square cut out from the center with dimensions 50 mm x 150 mm, Figure 3.3. The device is used to contain the water used to dissolve nitrate salts at the surface. To form a seal between the road and the nitrate collection device, plumber putty was used along the inside rim. Prior to testing, weight was applied to the top of the device to ensure a good seal with the pavement. 40ml of DI water, purified by a Thermo Scientific Barnstead Reverse Osmosis System, was injected into the sampling area and allowed to dissolve the salts for 5 minutes. The five-minutes soaking period was selected to avoid loss of the water via vertical pavement penetration and evaporation. After soaking, approximately 30 ml of the solution was extracted using a syringe. To avoid collection of dirt and debris from the pavement surface, the collected solution was passed through a 0.45 μm nylon filter.



Figure 3.3 Sampling of Nitrate on Photocatalytic Pavement Coating

3.3.3 Nitrate Laboratory Determination

Field samples were immediately transported to the laboratory for analysis and nitrate quantification. To quantify nitrate concentration in the collected samples, the colorimetric method of cadmium reduction with a Shimadzu UV Spectrophotometer 1800 was adopted (11). In this method, the cadmium metal is used to convert nitrite ions from nitrates into nitrites, which

then reacts with a reagent (chromotropic acid) to form a pink-colored solution. The intensity of color in the solution is proportional to the concentration of nitrate in the sample. The color intensity is measured by means of a UV Vis Spectrophotometer by measuring the amount of light absorbed at a 507 nanometer wavelength. The light absorption is then correlated to nitrate concentration by means of a standard calibration curve. An example of a calibration curve developed in this study to relate light absorption counts to nitrate concentration is presented in Figure 3.4.

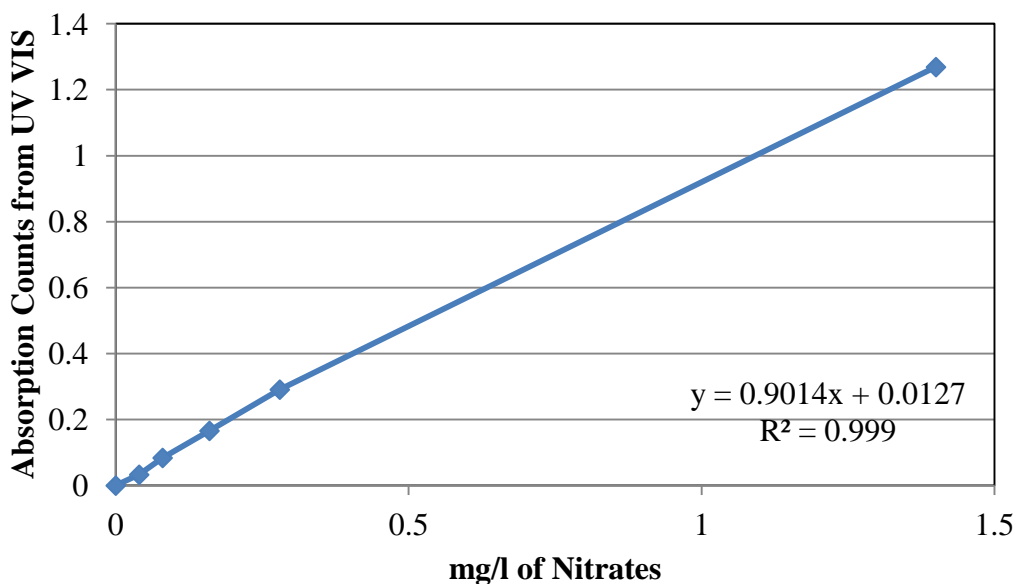


Figure 3.4 Standard Calibration Curve to Determine Nitrate Concentration Based on the Colorimetric Method

Given the direct relationship and mole equivalency between the oxidized nitrogen oxides and the deposited nitrates on the pavement surface (see Equations 1 and 2), the measured concentration of nitrates may be used to backcalculate the volume of pollutants oxidized in the atmosphere (ppmV). The EPA conversion method used in this analysis is summarized as follows (12):

1. **Step 1:** Convert nitrate concentration from mg/l to mole of NO/l knowing the molecular weight of NO_3^- and NO;
2. **Step 2:** Convert NO concentration from mol NO/l to mass of contaminants in g NO/l;

3. **Step 3:** Determine volume of NO contaminant in liter based on the ideal gas law as follows:

$$V_{\text{contaminant}} [\text{L}] = \frac{\text{Mass}_{\text{contaminant}} [\text{g}]}{\text{Molecular Weight}_{\text{contaminant}} \left[\frac{\text{g}}{\text{mol}} \right]} \times 8.3144 \left[\frac{\text{L.kPa}}{\text{mol.K}} \right] \times T_{\text{air}} \times \frac{1}{P_{\text{air}} [\text{kPa}]} \quad (3)$$

where,

$V_{\text{contaminant}}$ = volume of NO contaminant in liter;

$\text{Mass}_{\text{contaminant}}$ = determined from Step 2;

T_{air} and P_{air} = temperature and pressure of air; and

Other parameters are as previously defined.

4. **Step 4:** Convert volume of NO contaminant from liter to ppmV (ppmV = volume in ml/m³).

3.3.4 Laboratory Testing

NO removal efficiency determined in the field was compared to nitrogen oxide removal efficiency predicted in the laboratory for the same rate of photocatalytic coating applied on the same concrete substrate. The experimental setup used to collect the laboratory data was modified from the Japanese Industrial Standard (JIS TR Z 0018 “Photocatalytic materials – air purification test procedure”) (13), Figure 3.5.



Figure 3.5 Laboratory Experimental Test Setup

The laboratory procedure calls for each sample to be tested for a total time of six hours under UV-irradiation that is started after at least 180 minutes to ensure equilibrium concentrations. The environmental efficiency is calculated by analyzing the concentrations of NO, NO₂, and NO_x with the “lights on” compared to the difference in concentrations with the equilibrium at “lights off”(prior to “lights on”). Figure 3.6 illustrates the typical variation of NO_x concentration during the testing process. Testing was conducted at three levels of relative humidity (20, 50, and 80%). More details about the laboratory experimental setup have been presented elsewhere (3). Testing was conducted at room temperature as this is the standard test temperature in the JIS. It is noted in photocatalytic degradation, only large temperature differences such as the difference between summer and winter may affect the photocatalytic reaction with increasing temperatures helping the reaction.

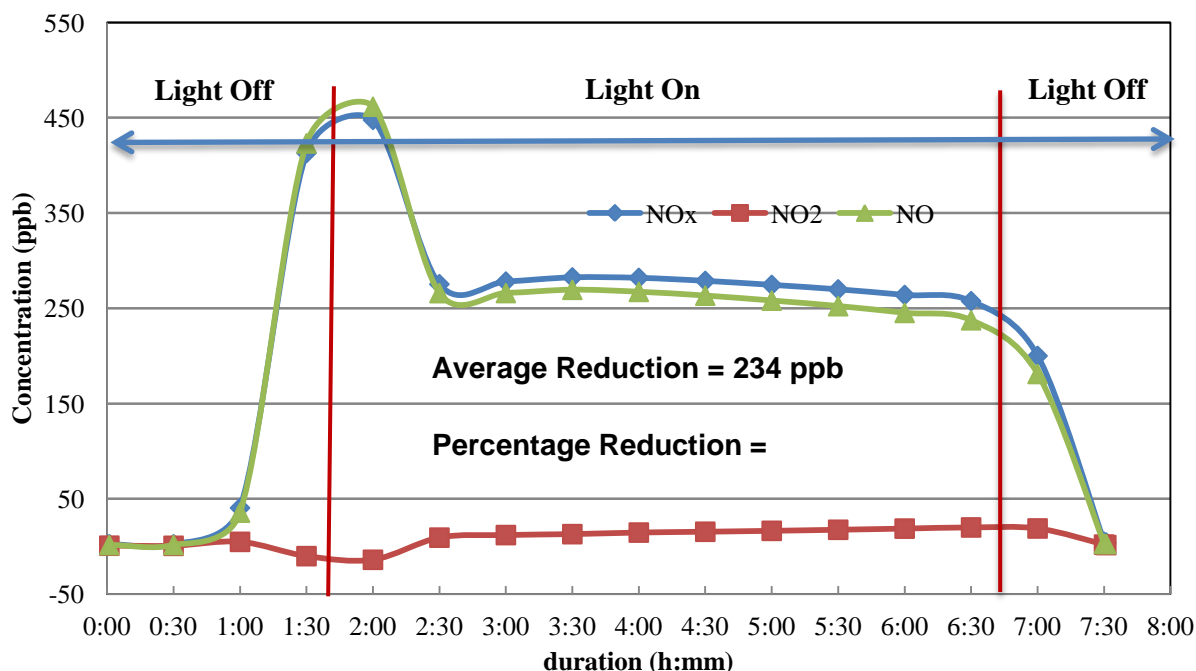


Figure 3.6 Typical Variation of NO_x Concentration during Laboratory Experiment

3.4 RESULTS AND ANALYSIS

Figure 3.7 presents the measured nitrate concentrations throughout the seven-days collection period. Concentrations shown in this figure reflect the concentrations after subtraction of the baseline concentrations measured at the beginning of the collection period. As shown in this figure, there is a definite indication that photocatalytic degradation of nitrogen oxide is taking place in the treated section. The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NO_x . The decrease in degradation of NO_x may be due that the surface have a carrying capacity of nitrates until the levels are abundant enough to prevent photocatalytic activity. NO_x levels in the ambient air also dropped significantly during the 7-days collection period. Figure 3.8 presents the NO_x levels according to the on-campus Louisiana Department of Environmental Quality air monitoring station. It is possible that the reduction of nitrates collected were due to the lower levels of NO_x in the ambient air and the accumulation of nitrates on the surface reducing the active sites available for photodegradation. Full regeneration of photocatalytic activity takes place through a self-cleaning process during rain event. Figure 3.9 presents the backcalculated volume of NO removed in the treated section from the atmosphere based on Equation (3).

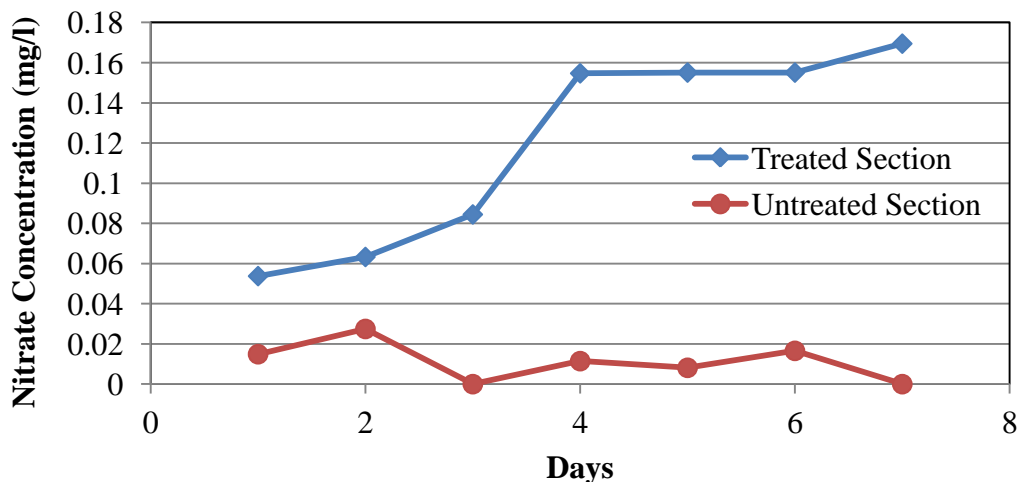


Figure 3.7 Nitrate Concentrations during the Seven-Day Collection Cycle

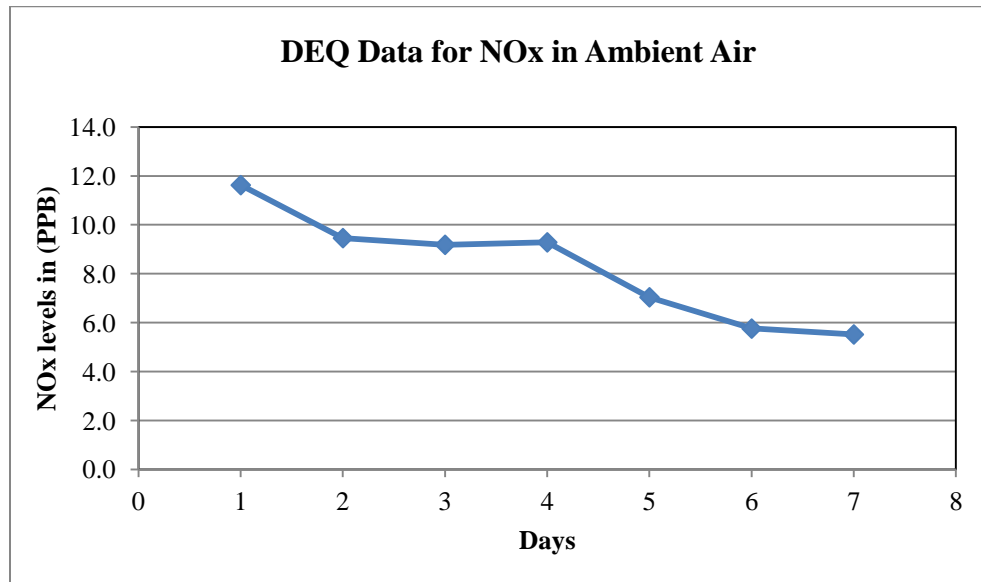


Figure 3.8 On-Campus DEQ Data for NO_x in Ambient Air during the Seven-Day Collection Cycle

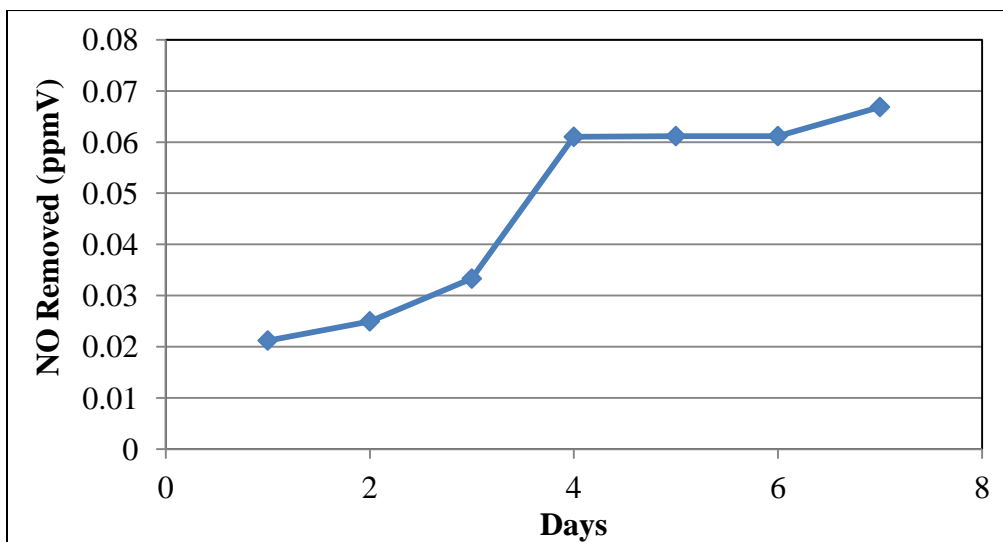


Figure 3.9 NO Removed in the Treated Section during the Seven-Day Collection Cycle

3.4.1 Coating Field Durability

The applied coating has been installed in December 2010. To assess the coating initial durability, the photocatalytic efficiency of the coating was compared 2 days after installation to

six months after installation. To compare the efficiency under the same environmental and operating conditions (i.e., traffic, wind, solar radiation, and relative humidity), two small areas were recently coated on the traffic lane and near the curb. NO reduction efficiency was compared six months after installation and 2 days after installation, see Figure 3.10 (the six-month data was not available for the area near the curb). As shown in this figure, six months of traffic and in-service operating conditions had negligible deterioration effects on photocatalytic efficiency. However, the efficiency of the coating was greater near the curb than in the traffic lane. This may be explained by tire traction in the traffic lane, which may collect a small level of nitrates and distribute them further up the road.

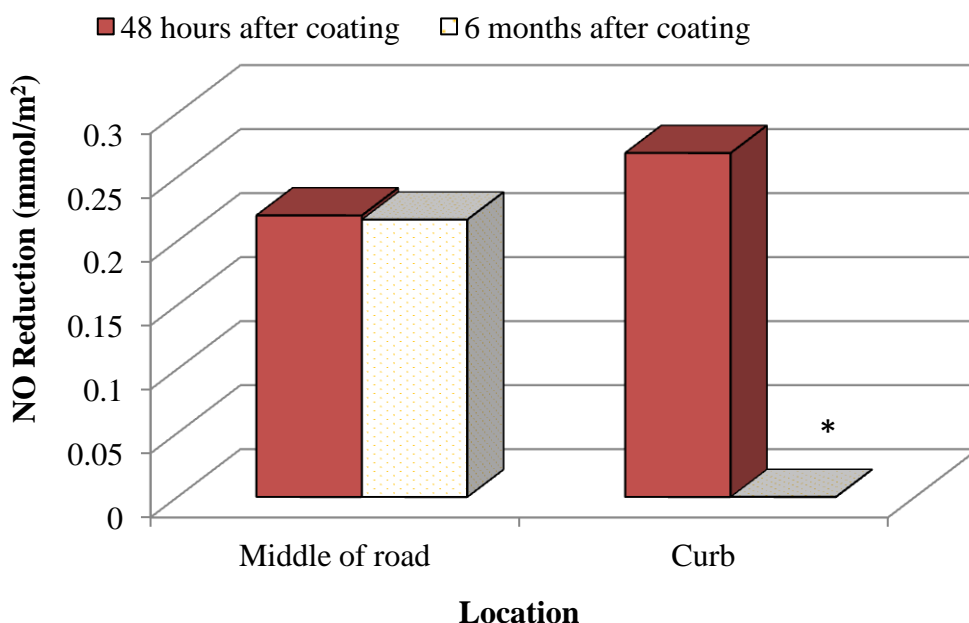


Figure 3.10 Comparison of NO reduction 48 hours after Application and Six Months after Application (*: Not Available)

3.4.2 Comparison of Field and Laboratory NO_x Removal Efficiency

Figure 3.11 compares the NO removal efficiency determined in the field one day after accumulation to the NO removal efficiency determined at different levels of relative humidity in the laboratory. The average relative humidity in the field during the collection period was 80%.

As shown in this figure, there was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity. Results in Figure 3.11 also show that humidity had a negative impact on NO_x reduction efficiency in the laboratory as the increase in relative humidity resulted in a decrease in NO_x removal efficiency. It is possible that at high relative humidity, the water molecules interfere with NO_x contact to the TiO₂ active sites on the surface. However, past research by the authors showed that at relative humidity lower than 25% humidity, the lack of water molecules required for the hydroxyl radicals hinders the photocatalytic oxidation (14).

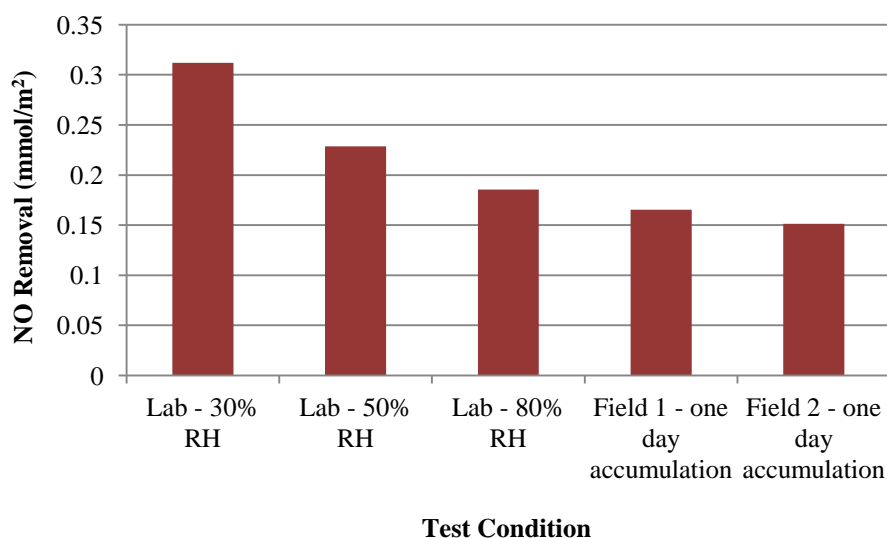


Figure 3.11 Comparison of NO Removal Efficiency in the Field and in the Laboratory

3.5 SUMMARY AND CONCLUSIONS

The US faces a significant challenge in controlling air pollution resulting from transportation activities and the growing population density. Validation of the effectiveness of photocatalytic pavements and their implementation in a manner that does not degrade the environment has the potential to expand use of this sustainable technology to mitigate many of the problems associated with pollution from motor vehicles. Results from this study are from the country's first air-purifying concrete photocatalytic pavements on Dec. 20, 2010. The test area is a pavement site located on LSU campus. The objective of this study is to validate field photocatalytic degradation of NO_x on the test site by measuring nitrate salts (NO₃⁻) deposited on

the pavement surface. By quantifying the nitrate levels produced in the field due to photocatalytic activity, measurements were correlated to laboratory test results of NO_x reduction efficiency. Based on the results of the experimental program, the proposed method to quantify photocatalytic efficiency through nitrate measurements was successful. In addition, the following conclusions may be drawn:

- There is definite evidence that photocatalytic degradation of nitrogen oxide is taking place in the field in the treated section. The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NO_x. Full regeneration of photocatalytic activity takes place in the field through a self-cleaning process during rain event.
- Six months of traffic and in-service operating conditions had negligible effects on the efficiency of the photocatalytic coating as compared to its efficiency just after installation.
- There was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity.

Based on the results presented in this study, further research is recommended to validate the long-term efficiency of the technology, the influence of environmental parameters such as solar radiation and temperature on NO removal efficiency, and to determine the influence of TiO₂ application rate on photocatalytic efficiency in the field. In addition, while this study focused on the photodegradation of NO_x, degradation of other pollutants is also recommended.

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CHAPTER 4

CONCLUSIONS AND FUTURE WORK

Validation of the effectiveness of photocatalytic pavements field performance is needed to address growing challenges associated with traffic pollution and population growth. Therefore, this study represents an essential step needed to expand use of this sustainable technology. In this study, Hassan and co-workers laid the country's first air-purifying asphalt and concrete photocatalytic pavements on Dec. 20, 2010. The test area is a pavement site located on LSU campus. Based on the results of this study, the following conclusions may be drawn:

- Results of the indirect methods of measuring photocatalytic degradation of NO_x show that there is evidence of a photocatalytic reaction occurring in the field.
- The photocatalytic process is very active during the first four days followed by a slight decrease in degradation rate of NO_x.
- Full regeneration of photocatalytic activity takes place in the field through a self-cleaning process during rain event.
- Six months of traffic and in-service operating conditions did not affect the efficiency of the photocatalytic coating as compared to its efficiency just after installation.
- There was a good agreement between NO removal efficiency measured in the field after one day of nitrate accumulation and in the laboratory experiment at the same level of relative humidity.
- Environmental factors impacting photocatalytic efficiency are wind speed and direction, light intensity, relative humidity, and solar radiation. However, due to the variability demonstrated in the results, additional factors such as vehicle activity and vehicle classification need to be considered.

Based on the results presented in this study, further research is recommended to validate the long-term efficiency of the technology, the influence of environmental parameters such as solar radiation and temperature on NO removal efficiency, and to determine the influence of TiO₂ application rate on photocatalytic efficiency in the field. In addition, future work quantifying the impact of photocatalytic pavements on the environment is needed.

APPENDIX

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David chose to further his education by taking courses in management practices, advanced software, environmental law and sustainability. David's passions include fulfilling his own purpose by helping to fulfill the purposes of other people, projects and ideas. Another passion of David's is to promote efficiency, effectiveness and simplicity in industry.