Nitrogen Oxide Reduction and Nitrate Measurements on TiO$_2$
Photocatalytic Pervious Concrete Pavement

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Abstract: Heterogeneous photocatalysis is considered one of the potential solutions for pollution remediation in which the natural decomposition process of harmful air pollutants is accelerated.

This process make use of photocatalytic agents like nano titanium dioxide. Nano titanium dioxide (TiO$_2$) has been found to have photocatalytic properties in which under UV light can oxidize and remove VOCs and NO$_x$ from the atmosphere. Therefore, the objective of this study is to evaluate the amount of nitrates released due to pervious photocatalytic concrete. To achieve this objective, samples were tested in the laboratory for photocatalytic Nitrogen Oxide (NO$_x$) reduction efficiency according to the Japanese Industrial Standard (JIS). After testing, samples were washed with deionized water to collect the nitrates deposited on the surface. The collected nitrate concentration was measured using colorimetric method (cadmium reduction). In addition, a parametric study was conducted to examine the performance of pervious photocatalytic concrete under different environmental conditions. Results showed that photocatalytic pervious concrete is capable of purifying ambient air from NO$_x$. In addition, a good agreement was obtained between the total amount of nitrogen compound eluted and the net amount of NO$_x$ removed under different mix design and environmental conditions. Results indicated that photocatalytic efficiency improved with the decrease in humidity, decrease in flow rate, and the increase in UV light intensity.

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Introduction

Man-made ambient air pollution originates from poisonous gases emitted by traffic and industrial activity. Traffic emissions include nitrogen oxide (NO$_x$), which is a significant urban pollutant in major US cities. The US Environmental Protection Agency (EPA) reported that the largest emissions of NO$_x$ originate from on-road motor vehicles [1]. In fact, 35% of NO$_x$, 60% of the carbon monoxide (CO), and 25% of volatile organic compounds (VOCs) were related to vehicular emission in the US in 2005 [1].

A solution to traffic air pollution is treatment of pollutants as close to the source as possible [2]. Since automobile emissions come in contact with the road surface, photocatalytic compounds such as TiO$_2$ can be used to construct air purifying pavements by integrating nano-TiO$_2$ within the pavement surface. Photocatalytic highway pavements can trap and decompose harmful pollutants including NO$_x$, which is converted to water soluble nitrates [3] Nitrogen monoxide (NO) is oxidized to NO$_2$-$^-$ (nitrate) and NO$_2$ is oxidized to NO$_3^-$ (nitrate), which is deposited on the pavement surface. The evidence of photocatalytic degradation of NO$_x$ can be measured using two methods: direct and indirect methods. The direct method involves measuring the reduction of NO$_x$ in the air while the indirect method involves quantifying the amount of nitrate deposited on the pavement surface using stoichiometry as it is a direct product of the decomposition of NO$_x$. The indirect method is best suited for field applications. In this case, the pavement surface is washed with deionized water to dissolve the nitrate ions, then the amount of NO$_3^-$ in the water is measured in the laboratory [4]. Recently, several laboratory studies have been performed in order to assess the de-polluting characteristics of TiO$_2$ photocatalytic compounds under conditions that simulate the actual highway environment including light intensity, temperature, relative humidity, and velocity of gas flow [3, 5, 6].

Pervious concrete contains the standard concrete constituents of aggregate, Portland cement, and water, but produce interconnected voids for water movement using gap-graded coarse aggregate [7]. The benefits of using pervious concrete include reduced stormwater runoff, cleaning of the stormwater through filtration and microbial degradation, and reduced potential for slipping [7, 8]. Recent studies have shown that pervious concrete stores less heat energy than traditional concrete pavement making it a cool pavement option for urban heat island mitigation [9, 10]. A natural progression for pervious concrete is to incorporate photocatalytic agents to provide air cleaning ability along with the already existing stormwater management and urban heat island benefits. The lighter color of photocatalytic cement (caused by the addition of white TiO$_2$) causes an alleviated albedo from photocatalytic agents, which would further reduce the heat island effects through lower surface temperatures [11]. Hassan and co-workers successfully evaluated

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the effectiveness of photocatalytic pervious concrete in the laboratory [12]. Results indicated that laboratory NO$_x$ removal efficiency for pervious concrete samples was superior to regular impervious concrete samples. Therefore, the objectives of this study are to quantify the amount of nitrates that are released due to photocatalytic compound used in the preparation of pervious concrete and to study the effect of different environmental parameters on the photocatalytic efficiency. To achieve these objectives, pervious concrete samples were tested in the laboratory for photocatalytic NO$_x$ reduction efficiency according to JIS standards. Testing was conducted under different environmental and operational conditions including flow rate, UV intensity, temperature, and relative humidity. To quantify the amount of nitrates released due to photocatalytic activities, the colorimetric method of cadmium reduction with a Shimadzu UV Spectrophotometer 1800 was adopted. To validate the experimental results obtained by colorimetric method, the amount of NO$_x$ removed by the test piece due to photocatalytic action was compared to the nitrogen compound eluted from the test piece.

**Background**

The impulse of the use of TiO$_2$ was suggested by Fujishima and Honda in 1972 [13]. TiO$_2$ produces hydroxyl radicals and superoxides, which are responsible for oxidizing and reducing environmental contaminants including VOCs and NO$_x$ in the presence of UV light [14]. The following equations describe a suggested mode of oxidation of NO$_x$ via hydroxyl radical intermediates in the presence of the photocatalyst [2]:

\[
NO + OH \xrightarrow{\text{TiO}_2} NO_3 + H^+
\]  

\[
NO_2 + OH \xrightarrow{\text{TiO}_2} NO_3 + H^+
\]

The potential of TiO$_2$ as an air purifier in urban and metropolitan areas, which suffer from high concentration of air pollutants, have been widely recognized in the literature [5-6; 15-16]. Being produced in a powder form, a number of research studies have suggested to use it in a thin film form and to apply it as a coating or slurry to various types of substrates [17]. Titanium dioxide have also been evaluated and patented as a coating to concrete paving materials, an environmentally-friendly cement, an architectural concrete (white cement), a facade to buildings, and as concrete tiles [18; 19]. One study suggested that the use of titanium dioxide in combination with a cementitious material improves SO$_2$ removal efficiency through action of the alkaline substratum [20]. It was reported that the efficiency of this technology depends on many factors including the size of the surface exposed, the concentration of pollutants, humidity, and ambient temperature [6].

While it is generally assumed that the concentrations of water-soluble nitrates produced as a result of the photocatalytic oxidation would be low, this assumption has not been validated in pavement applications [21]. Effects of nitrogen pollution are diverse and far-reaching. Not only nitrogen pollution affects human health and the environment, but its cascading effects (such as the need for additional treatment for drinking water or increases in health care costs for related illnesses) cost millions of dollars per year, directly impacting the economy [1]. The contamination of water with excessive quantities of nitrogen is also a growing concern in the US.

**Experimental Program**

**Laboratory Samples**

The experimental program evaluated the effects of void ratio and photocatalytic depth on air quality of pervious concrete samples prepared with photocatalytic cement. The specimen design consisted of two lifts, the bottom lift is pervious concrete and the top lift is photocatalytic pervious concrete [22]. The experimental program tested 21 samples with varied void ratios (23, 27, and 31%) and varied photocatalytic depths (0.5 in. (12.7 mm), 1 in. (25.4 mm), 2 in. (50.8 mm), and 3 in. (76.2 mm)). Since nitrate salt is a direct product of photocatalytic activity, laboratory measurements were conducted in this study to quantify the amount of nitrate deposited on the specimen surface. Nitrate salts deposited on the pavement were measured for all 21 samples. The bottom lift of standard pervious concrete was poured and followed immediately by the upper photocatalytic layer using a wet-on-wet method [22]. Fresh concrete was pre-weighed before placing to control unit weight and voids. The adopted pervious concrete mix design was intended to perform dual function for both storm water and air quality improvements by using specialty photocatalytic Portland cement. To minimize the use of photocatalytic cement, the samples were prepared in two lifts: the bottom lift of standard pervious concrete was poured and followed immediately by the upper photocatalytic layer using a wet-on-wet method. The mixture proportions associated with each particular void content and TiO$_2$ depth are shown in Table 1. Test specimens were prepared in triplicates with dimensions of 10 in. (25.4 cm) x 10 in. (25.4 cm) x 3 in. (7.62 cm) as shown in Fig. 1. A full description of the photocatalytic concrete field study has been presented elsewhere [4].

**Laboratory Testing**

The experimental setup used to collect the laboratory data was based on the Japanese Industrial Standard (JIS TR Z 0018 “Photocatalytic materials – air purification test procedure”) [23]. The developed experimental setup consisted of a pollutant source, zero air source, calibrator, humidifier, photoreactor, and chemiluminescent NO$_x$ analyzer as shown in Fig. 2. The setup simulates different environmental conditions by allowing for control
Fig. 1. Illustration of Pervious Concrete Samples.

Fig. 2. Illustration of the Experimental Laboratory Setup.

Fig. 3. Variation of NO\textsubscript{x} Concentration during the Environmental Experiment.

The environmental efficiency of the prepared pervious concrete in removing NO\textsubscript{x} pollutants from the air stream was evaluated at different levels of pollutants’ flow rates, relative air humidity, temperature, and UV light intensities. Fig. 3 illustrates the variation of NO\textsubscript{x} concentration during the course of a typical environmental experiment for the 3 in. (76.2 mm) TiO\textsubscript{2} depth with 31% void ratio (30% humidity, 3 L/min flow rate, and 2 mW/cm\textsuperscript{2} UV intensity). The UV light is turned on 1 hour after the start of the experiment in order to ensure mostly equilibrium conditions. The inlet concentration reached equilibrium at 450 ppb before the light was turned on. After the light is turned on, a fast drop of NO concentration in the outlet air stream is exhibited and NO\textsubscript{2} is created from the NO oxidation. During the photocatalytic experiment, NO\textsubscript{x} concentration slightly increased. After 5 hours of testing, the light and gas supply was turned off allowing for any desorption to occur. For the test condition shown in Fig. 3, the use of TiO\textsubscript{2} photocatalytic pervious concrete had NO removal efficiency of 78% and the overall NO\textsubscript{x} reduction was 75%. The variation of NO\textsubscript{x} concentration was obtained for each tested sample in the experimental program and the NO removal efficiency for each case was calculated and is presented in the results section.

Environmental Parametric Study

To evaluate the effects of different environmental parameters including pollutant flow rate, UV intensity, humidity, and temperature on photocatalytic efficiency and the amount of associated nitrate, a partial factorial design was conducted. The concrete sample with 3 in. (76.2 mm) TiO\textsubscript{2} depth and 31% void ratio was selected for the paramedic study since it showed the higher NO\textsubscript{x} reduction efficiency. Three levels were considered for each factor and nine combinations were tested with three replicas to account for variability. Table 2 presents the nine combinations considered in the parametric study.

Nitrate Laboratory Sampling

As previously noted, the indirect method was utilized in this study to measure the nitrate ions accumulated on the pavement surface. While this method can easily be implemented in the field, its main disadvantage is that the nitrate ions may not be completely eluted in the washes. Since nitrate salt is a direct product of photocatalytic activity (see Eq. 2), laboratory measurements were conducted to quantify the amount of nitrate deposited on the pavement surface. Nitrate salts deposited on the surface were measured for 21 samples (Table 1) with different mix constituents. To measure the amount of deposited nitrate on the specimen surface, all the samples were initially washed with deionized water based on the JIS standard to remove any existing nitrates from the surface. A nitrate baseline collection cycle was conducted on all samples before the start of the photocatalytic test. A Plexiglas container with dimensions 12 in. (30.48 cm) × 12 in. (30.48 cm) × 4 in. (10.16 cm) was fabricated and used to soak the samples. To collect the deposited nitrate on the specimen surface, all the samples were initially washed with deionized water. To get a uniform concentration, the collected solution was stirred rigorously. Three water samples were then collected and filtered through a 0.45 μm nylon filter after each soak in order to determine the variability in the solution.

Nitrate Laboratory Determination

To quantify nitrate concentration in the collected water samples, the
where,

\[ Q_w = Q_{w_1} + Q_{w_2} = V_{w_1} \left( [NO_3^-]_{w_1} / 62 \right) + V_{w_2} \left( [NO_3^-]_{w_2} / 62 \right) \]  (3)

and

\[ W_1 \text{ and } W_2 \text{ are the first and second DI washes, respectively.} \]

During the experiment, NO\textsubscript{x} introduced into the photocatalytic chamber will undergo four transformations, adsorption by the photocatalytic pervious sample, conversion to nitrate, conversion to nitrogen dioxide, and desorption by the test piece. The amount of NO\textsubscript{x} converted into nitrates can be calculated using the steps defined in the JIS [23]. The flow rate was corrected for Standard Temperature and Pressure (STP) conditions using the combined gas law as follows [24]:

\[ SCF = ACF \left( \frac{P_{\text{actual}}}{P_{\text{standard}}} \right) \left( \frac{T_{\text{standard}}}{T_{\text{actual}}} \right) \]  (4)

where,

\[ SCF = \text{the standard condition flow rate;} \]
\[ ACF = \text{actual test condition flow rate,} \]
\[ P = \text{the absolute pressure unit (kPa); and} \]
\[ T = \text{the absolute temperature unit (K) - STP assumes T is 273 K and P is 101.3 kPa.} \]

**Results and Analysis**

The variation of NO\textsubscript{x} and NO removal efficiency with different void ratios and TiO\textsubscript{2} depths was evaluated. Fig. 5 presents the effect of void ratios and depths of TiO\textsubscript{2} on NO\textsubscript{x} and NO concentration for the pervious concrete samples tested at 30% humidity, UV intensity of 2 mW/cm\textsuperscript{2}, and 3 L/min pollutant flow rate. As shown in this figure, NO and NO\textsubscript{x} removal efficiency increased as the depth of the photocatalytic layer increased. Results showed an average NO\textsubscript{x} reduction efficiency of 6% for control sample, 30% for the 0.5 in. (12.7mm) of TiO\textsubscript{2} depth samples. This can be explained by the fact that with pervious pavements, UV light can infiltrate to greater TiO\textsubscript{2} depth enhancing the photocatalytic efficiency of the sample. The highest environmental performance was obtained from the sample with 3 in. (76.2 mm) TiO\textsubscript{2} depth and 31% void ratio.

Fig. 6 presents the measured nitrate concentrations based on the cadmium reduction method for different mix design of pervious concrete samples. Baseline concentrations were subtracted from the concentrations quantified after the test by washing the sample with DI water based on the JIS standards as described above. Error bars in the figure show ±10% deviation from the mean value. As shown in this figure, photocatalytic degradation of NO\textsubscript{x} is evident based on nitrate measurements and there is a direct relationship.
between nitrate concentration and TiO$_2$ thickness. Larger TiO$_2$ depth results in more photocatalytic degradation of nitrogen oxide and produces more nitrates on the surface.

Results of the cadmium reduction method were compared to the net amount of NO$_x$ removed by the photocatalytic action. The net amount of NO$_x$ removed by the photocatalytic action was calculated based on the JIS standards. Fig. 7 compares the net amount of NO$_x$ removed by the test piece to the total amount of nitrate eluted from the test piece for different pervious concrete samples. Concentrations shown in this figure reflect the concentrations after subtraction of the baseline concentrations measured after washing the sample with DI water. As shown in this figure, there is a good agreement between the results of both methods. From these results, it can be concluded that measuring the nitrate ions accumulated on the surface is an adequate method to quantify NO$_x$ reduction efficiency.

**Environmental Parameters Test Results**

A parametric study was carried out to study the variation of NO$_x$ and NO removal efficiency under different environmental conditions (Table 2). Results showed the average NO$_x$ removal efficiency of three samples with 3 in. (76.2 mm) of TiO$_2$ depth and 31% void ratio test under different environmental conditions. The sample with 3 in. (76.2 mm) of TiO$_2$ depth and 31% void ratio was selected since it showed the highest NO and NO$_x$ removal efficiency under the control conditions as shown in Fig. 5.
presented in Table 2, test number 8 (Flow rate of 3 L/min, UV intensity of 2 mW/cm², 23°C temperature, and 30% humidity) showed the highest average NO and NO\textsubscript{x} removal efficiency and test number 1 (Flow rate of 9 L/min, UV intensity of 0.8 mW/cm², 50°C temperature, and 80% humidity) showed the lowest NO and NO\textsubscript{x} removal efficiency. The highest NO\textsubscript{x} reduction occurred at the lowest relative humidity, medium UV intensity, lowest temperature, and lowest flow rate while the lowest NO\textsubscript{x} reduction efficiency occurred at the highest relative humidity, lowest UV intensity, highest temperature, and highest flow rate. More details about the effects of environmental parameters for regular and pervious concrete have been presented elsewhere [6, 25].

To quantify the nitrate deposited on the specimen surface (3 in. (76.2 mm) of TiO\textsubscript{2} depth and 31% void ratio), the cadmium reduction test was conducted for the 9 different run combinations outlined in Table 2. Fig. 8 presents the measured nitrate concentrations based on the cadmium reduction method for the different environmental conditions. This figure reflects different levels of photocatalytic activity at different environmental conditions. As shown in this figure, for the test number 1, which was conducted at high relative humidity, low UV intensity, and high pollutant flow rate, the nitrate concentration is almost zero, which means that photocatalytic action is almost insignificant under these conditions (1%). On the other hand, test number 8 showed the highest nitrate concentration. These results validate that the variation in nitrate concentrations at the surface is an indication of the level of photocatalytic activities under different environmental conditions.

Fig. 9 compares the net amount of NO\textsubscript{x} removed by the test sample to the total amount of nitrate eluted from the test sample under different test conditions. The concentrations shown in this figure reflect the concentrations after subtraction of the baseline concentrations measured after washing the sample with DI water based on JIS standards. As shown in this figure, there is a good agreement between the total of nitrate eluted and the net amount of NO\textsubscript{x} removed. The error was less than 5%.

Fig. 8. Measured Nitrate Concentrations Based on the Cadmium Reduction Method for the Different Test Runs.

Fig. 9. Comparison between the Nitrate Equivalent Calculated from NO\textsubscript{x} Measurements and the Nitrate Deposited at the Surface after Six Hours of Photocatalytic Activity for the Different Test Runs.

Conclusions

Validation of the effectiveness of photocatalytic pavements and their implementation in a manner that does not damage the environment has the potential to expand the use of this sustainable technology to mitigate many of the problems associated with pollution from motor vehicles. The objectives of this study are to quantify the amount of nitrates that are released due to photocatalytic compound used in the preparation of pervious concrete and to study the effect of different environmental parameters on the photocatalytic efficiency. Based on the results of this study, the following conclusions were drawn:

- TiO\textsubscript{2} was effective in removing NO\textsubscript{x} pollutants from the air stream with an efficiency ranging from 30 to 70%. The maximum NO\textsubscript{x} removal efficiency was achieved at a 3 in. (7.62 cm) depth of TiO\textsubscript{2} with a 31% void ratio.
- At high relative humidity, low UV intensity, high flow rate, and high temperature, the measured nitrate concentration was almost zero, which means that photocatalytic activity is almost insignificant under these environmental conditions.
- The highest NO\textsubscript{x} reduction occurred at the lowest relative humidity, medium UV intensity, lowest temperature, and lowest flow rate while the lowest NO\textsubscript{x} reduction efficiency occurred at the highest relative humidity, lowest UV intensity, highest temperature, and highest flow rate.
- There was a good agreement between the total of nitrogen
compound eluted and the net amount of NO₃ removed under different mix design and environmental conditions.

- These results validate that the variation in nitrate concentrations is a good indicator of the level of photocatalytic activities under different environmental conditions.

Based on the results presented in this study, further research is recommended to validate the long-term efficiency of the technology in the field, including long-term environmental performance durability.

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