

**Self Cleaning Coatings for Graffiti Prevention Removal and De-Pollution  
(Demo Project)**

FINAL REPORT  
January 2012

Submitted by

Perumalsamy Balaguru, Ph.D.  
Professor of Engineering  
Rutgers University

Jeremy Brownstein, M.S.  
Graduate Assistant  
Rutgers University

Matthew Klein, M.S.  
Graduate Assistant  
Rutgers University



NJDOT Research Project Manager  
Stefanie Potapa

In cooperation with  
New Jersey  
Department of Transportation  
Bureau of Research

And

U.S. Department of Transportation  
Federal Highway Administration

## **DISCLAIMER STATEMENT**

“The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the New Jersey Department of Transportation or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.”

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

TECHNICAL REPORT  
STANDARD TITLE PAGE

1. Report No. FHWA-NJ-2012-007		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Self Cleaning Coatings for Graffiti Prevention Removal and De-Pollution (Demo Project)			5. Report Date January 2012		
			6. Performing Organization Code CAIT/Rutgers		
7. Authors Balaguru, Perumalsamy Ph.D., Brownstein, Jeremy M.S., and Klein, Matthew M.S.			8. Performing Organization Report No. FHWA-NJ-2012-007		
9. Performing Organization Name and Address Rutgers, The State University of New Jersey Center for Advanced Infrastructure and Transportation (CAIT) 100 Brett Road Piscataway, NJ 08854			10. Work Unit No.		
			11. Contract or Grant No.		
12. Sponsoring Agency Name and Address New Jersey Department Of Transportation PO Box 600 Trenton, NJ 08625		Federal Highway Administration U.S. Department of Transportation Washington, D.C. 20590		13. Type of Report and Period Covered Final Report 10/15/2007 – 10/31/2012	
				14. Sponsoring Agency Code	
15. Supplementary Notes  U.S. Department of Transportation/Research and Innovative Technology Administration (RITA) 1200 New Jersey Avenue, SE Washington, DC 20590-0001					
16. Abstract The primary focus of this report is to demonstrate the suitability of an inorganic polymer composite coating for transportation related structures. This report presents the results of three field applications and evaluation of graffiti resistance including removal techniques, self cleaning and de-pollution properties. For field applications, pigment combinations were developed to match the colors of existing structures or to blend with the surrounding areas. Techniques were developed and refined for application of the coating. To determine the effectiveness of graffiti resistance, several methods were assessed. Citric based cleaner and baking soda pressure washer were found to be most effective. The results show that the coating effectively cleans organic pollutants and the results compare well with those reported for anatase titanium dioxide containing concrete and mortar. The exposure from the sun in the field was successfully simulated in the lab using UV light. Based on the results obtained it can be concluded that the composite coating is ready for large scale field applications.					
17. Key Words Inorganic Coating, High-Temperature, Self Cleaning, De-pollution			18. Distribution Statement		
19. Security Classif (of this report)  Unclassified		20. Security Classif. (of this page)  Unclassified		21. No of Pages  57	22. Price

## **ACKNOWLEDGEMENTS**

The authors wish to thank Ms Stefanie Potapa, Ms Camille Crichton- Sumners, Mr. Robert Sasor and Paul Pospiech for their contribution and encouragement. The contribution of Rutgers Staff and students are also acknowledged.

## TABLE OF CONTENTS

	Page
INTRODUCTION.....	1
BACKGROUND INFORMATION.....	2
Basic Features of Inorganic Polymer Composite .....	2
Review of Existing Graffiti Resistant Coatings .....	3
<u>Sacrificial Coatings</u> .....	3
<u>Permanent Coatings</u> .....	3
<i>Inorganic Polymer Coating</i> .....	3
<i>Semi-Permanent Coatings</i> .....	4
<i>Non-Stick Surfaces</i> .....	4
<u>Graffiti Resistant Products Survey</u> .....	4
<i>Data Analysis</i> .....	5
<i>Permanent vs. Sacrificial Coatings</i> .....	5
<i>Organic vs. Inorganic</i> .....	5
<i>Number of Coats</i> .....	6
<i>Cleaning Procedures</i> .....	6
<i>Durability Studies</i> .....	6
<i>DOT Field Demonstrations</i> .....	6
<i>Self Cleaning and Depolluting Systems</i> .....	7
Durability of the Proposed Coating System .....	7
FIELD APPLICATIONS .....	8
Color Schemes.....	9
Route 280 Retaining Wall Project.....	9
<u>Additives and Application Methods</u> .....	9
<u>Color</u> .....	10
<u>Details of Field Application</u> .....	11
<u>Summary</u> .....	12
Woodbridge Mall Retaining Wall - Route 1 .....	14
<u>Color</u> .....	14
<u>Application</u> .....	14
<u>Summary</u> .....	15
Milltown Abutment – Route 1.....	17
<u>Application</u> .....	17
<u>Summary</u> .....	18
EVALUATION OF GRAFFITI REMOVAL METHODS.....	19
Coating Types Summary.....	19
Laboratory Results .....	20
<u>Citrus Solution and Cold Water</u> .....	20
<u>Hot Water</u> .....	21
<u>Cold Water Power Washer and Citrus Solution</u> .....	22
<u>Hot Water Power Washer</u> .....	23
<u>Hot Water Power Washer and Citrus Solution</u> .....	24
<u>Use of Baking Soda (Abrasive) with Hot Water</u> .....	24
SELF CLEANING PROPERTIES .....	25
State-Of-The-Art.....	26

Test Setup .....	26
<u>Indoor Tests</u> .....	26
<u>Outdoor Tests</u> .....	27
Test Results .....	27
<u>48-Hour Test Results - Indoor</u> .....	27
<u>48-Hour Test Results - Outdoor</u> .....	28
<u>Livingston Lab Results</u> .....	29
<u>Woodbridge Mall Retaining Wall - Route 1 Results</u> .....	30
<b>EVALUATION OF DEPOLLUTING CHARACTERISTICS</b> .....	32
State-of-the-Art .....	32
Mechanism .....	33
<u>Air Purification</u> .....	35
<u>NO Absorption of TiO<sub>2</sub></u> .....	36
<u>Reaction Variables</u> .....	36
<u>Effect of UV-Light Intensity</u> .....	36
Research Program.....	37
Test Setup .....	37
Results.....	38
<u>Indoor Test Results</u> .....	38
<i>Nitric Oxide Reduction</i> .....	38
<i>Nitrogen Dioxide Reduction</i> .....	40
<u>Outdoor Test Results</u> .....	43
<i>Nitric Oxide Reduction</i> .....	43
<i>Nitrogen Dioxide Reduction</i> .....	45
<u>UV versus Sunlight</u> .....	46
<u>Presence of TiO<sub>2</sub></u> .....	46
<u>Initial Concentration of NO and NO<sub>2</sub> gases</u> .....	46
<b>CONCLUSIONS</b> .....	47
Demonstration Projects .....	47
Graffiti Resistance .....	48
Self Cleaning .....	48
Depollution.....	48
<b>REFERENCES</b> .....	50

<b>LIST OF FIGURES</b>	<b>Page</b>
Figure 1. a) Close-up and b) From a Distance .....	10
Figure 2. Contrast between Parent and Coated Surfaces.....	11
Figure 3. 200x Magnification of Coating Surface.....	12
Figure 4. Condition After Coating.....	13
Figure 5. Condition after 2 Years .....	14
Figure 6. Detail of Coating.....	15
Figure 7. Condition after Application .....	16
Figure 8. Condition after 1 Year .....	16
Figure 9. Graffiti at the Milltown Site .....	17
Figure 10. Coated Milltown Bridge Abutment.....	18
Figure 11. Demonstration of Paint Removal .....	18
Figure 12. Before and After .....	21
Figure 13. Before and After .....	22
Figure 14. Before and After .....	23
Figure 15. Before and After .....	23
Figure 16. Before and After .....	24
Figure 17. Before and After .....	25
Figure 18. (a) Setup for Rhodamin B Tests and (b) Rhodamin B Dot .....	27
Figure 19. 48-Hour Indoor Tests .....	28
Figure 20. 48-Hour Outdoor Tests .....	29
Figure 21. Livingston Lab Test Results.....	30
Figure 22. Woodbridge Mall Retaining Wall - Route 1 Test Results .....	31
Figure 23. Woodbridge Mall Retaining Wall - Route 1 Wall with Rhodamin B Dot	31
Figure 24. Setup for Indoor Depollution Tests .....	38
Figure 25. 30 ppm Nitric Oxide Gas Concentration (Indoor) .....	39
Figure 26. 60 ppm Nitric Oxide Gas Concentration (Indoor) .....	40
Figure 27. 30 ppm NO <sub>2</sub> Gas Concentration (Indoor).....	41
Figure 28. 60 ppm NO <sub>2</sub> Gas Concentration (Indoor).....	42
Figure 29. 30 ppm NO Gas Concentration (Outdoor).....	44
Figure 30. 60 ppm NO Gas Concentration (Outdoor).....	45

## INTRODUCTION

Results presented in this report are related to the development of an inorganic polymer composite coating for the protection of concrete structures. Unique properties of this composite include: high temperature resistance, high abrasion resistance, self cleaning and de-polluting properties. The composite is also very conducive for application in terms of workability and the absence of volatile organic compounds during mixing, application and curing. The composite adheres well to concrete, brick, and timber surfaces. The results presented in this report focuses on field application, evaluation of graffiti removal methods, and self cleaning properties.

The Background Information section features a compilation of information on the existing and commercially available graffiti resistance coating systems. Experiences of various state transportation departments concerning approved graffiti removal systems are also presented in this section.

The results gathered during three different field application projects are organized in the Field Applications section. The objectives of the project, details about the application of the inorganic coating, the color schemes used and subsequent monitoring of the projects are presented for all the three field applications.

The Evaluation of Graffiti Removal Methods section outlines six different graffiti removal techniques attempted on the inorganic coating and the results of each trial test. These tests include the use of a citrus-based cleaner with cold water, hot water, and several power washer tests.

The results of the self cleaning tests can be found in the Self Cleaning Properties section. These tests were conducted both inside the laboratory using an ultra-violet (UV) light bulb and outside using sunlight. The tests were conducted either over a 48-hour period or over a one month period.

The Evaluation of De-pollution Characteristics section explains how the reduction in gases such as nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) occur and then how to test the rate of reduction for each of these gases in the de-pollutions tests. This section also explores the effect that certain variables will have on the rate of reduction such as the initial concentration of gas, UV light bulbs vs. sunlight, and the presence of titanium dioxide (TiO<sub>2</sub>) or zinc oxide (ZnO).

The conclusions drawn from this study are presented in the last section. In summary, the inorganic composite is a viable product for creating a graffiti resistant, self cleaning, and de-polluting coating.



## BACKGROUND INFORMATION

Civil structures, including those related to the transportation system, naturally lend themselves to vandalism and various environmental elements of environments. Concrete walls and abutments are used as canvasses for a variety of unwanted artwork and territorial markings for gangs as well as being the settling place for the pollutants generated by most motor vehicles on the road today. Due to the rough surface of concrete faces, cleaning them is often challenging and costly.

Thus, there is a demand for concrete coatings that are resistant to paint and pollution and can reduce cleaning time. The inorganic matrix coating has a hard smooth surface that lends itself for easy removal of graffiti. In addition, this coating has also self-cleaning and de-polluting capabilities. Background information presented in this section, focuses on the basic features of the inorganic polymer and how it compares with other composites and coatings that are available in the market.

### Basic Features of Inorganic Polymer Composite

The basic features of this material are as follows:

- The cementing component is potassium alumina-silicate, or polysialate-silox with the general chemical structure:



where  $z \gg n$  and  $n$  is the degree of poly-condensation;  $z$  is 1, 2, and 3; and  $w$  is the binding water amount.

- The resin is prepared by mixing a liquid component with a potassium-poly (sialate-siloxo) powder to a plastic consistency with the resulting mixture referred to as a matrix. Fillers and hardening agents can be added to the powder component to enhance the matrix properties.
- The matrix is water based; consequently, tools and spills can be cleaned with water. All of the components are nontoxic and no fumes are emitted during mixing or curing.
- The pot life varies from 30 minutes to 3 hours for compositions that cure at room temperature.
- Common application procedures such as brushing, rolling, and spraying are compatible with the matrix.

- The matrix can withstand temperatures up to 1000°C, and is not affected by UV radiation. Fire tests show that the flame-spread index is zero.
- The base coating material is white and hence other color schemes can be easily formulated using pigments.
- The system is compatible with brick, concrete, wood, and steel.
- Self cleaning and de-polluting properties are provided by a zinc oxide filler. <sup>(1)</sup>

## **Review of Existing Graffiti Resistant Coatings**

Graffiti resistant products available in the market can be divided into two broad categories, namely: sacrificial and permanent coatings. In the following sections, descriptions of these two types of coatings are presented.

### **Sacrificial Coatings**

Sacrificial coatings are generally a wax-like polymer coating that is sprayed or mixed with water and then applied to surfaces that are vulnerable for to graffiti. When the structure is tagged by graffiti, the sacrificial coating along with everything on top of it is removed. The typical method for removal is melting off the coating and graffiti with hot water under pressure. Once the surface has dried, the sacrificial graffiti-resistant coating is then re-applied. The use of sacrificial coatings can be expensive and is very time consuming since it takes time to coat a surface and then remove and reapply a new coat every time it is marked with graffiti. The coated wall also appears to be old.

### **Permanent Coatings**

Permanent coatings provide a long term solution to problems with graffiti. Most of the existing coating formulations are organic and generally use the same chemicals that are used for non-stick cookware. Soiling and graffiti can be removed from these surfaces using high pressure water or some form of chemical. In most cases, the company that manufactures and/or distributes the coating will recommend a graffiti removal method. The company's recommendation sometimes includes the use of chemicals patented by the company and designed to work well with their coating system. The various chemicals used in graffiti removal for permanent coating are claimed to be benign and do not have any harmful effects to the environment.

### ***Inorganic Polymer Coating***

The inorganic polymer coating developed at Rutgers University provides a glassy hard surface and lends itself as a graffiti resistant coating. This quality was discovered in a previous study using a fiber reinforced inorganic polymer composite as a protective

coating for transportation related infrastructures. <sup>(2)</sup> The unique features of this coating are as follows:

- The matrix used in the composite is inorganic, making it resistant to fire and UV light. <sup>(3)</sup>
- The system is water-based and has no toxic substances. In addition, no toxins are released during mixing, application, or curing.
- The coating can be applied with minimum surface preparation.
- The permeability of the coating material is much less than the permeability of concrete but it allows the release of vapor pressure build-up; therefore, the coating does not delaminate from the parent surface. <sup>(4)</sup>
- The matrix is compatible with concrete, brick, steel and wood.
- The matrix cures to a glassy texture and hence organic paints do not adhere to the coated surfaces.

### ***Semi-Permanent Coatings***

Semi-permanent coatings are commonly based on acrylics or cross-linking systems, such as epoxy, urethane, or polyester. These coatings are called semi-permanent because they can withstand the use of chemicals for graffiti removal, a few times before the coating wears out and must be removed or recoated. Aggressive chemical removers are necessary to remove the graffiti and after each use the graffiti resistance becomes weaker making removal more difficult.

### ***Non-Stick Surfaces***

Non-stick systems are pre-manufactured anti-graffiti systems. They cannot be applied by painting or spraying. Installing non-stick surfaces can be costly and time consuming. If damaged, the system must be replaced anew. The main types of non-stick systems are Fluorine and Silicon based systems. These systems are not suitable for transportation infrastructures and therefore are not discussed in this report.

### **Graffiti Resistant Products Survey**

The primary sources for this survey were: published literature, web-search, and the material collected by the New Jersey Department of Transportation (NJDOT). First, all the information was collected and synthesized in a relatively uniform format. Then the information was analyzed to obtain information on:

- Type of coating related to permanency
- Number of constituent components
- Cost (if available)
- Type of graffiti removal
- Durability study
- Field demonstrations with various transportation agencies in USA
- Experience of transportation agencies

### ***Data Analysis***

The following literature review led to the identification of various products that are currently being used by the Departments of Transportation transportation departments in different states for their graffiti resistant properties. Many of these states also use products that remove graffiti without the use of any coating. In most cases the company that supplies the coating material also supplies the cleaning liquid.

### ***Permanent vs. Sacrificial Coatings***

There were 41 permanent and 6 sacrificial coatings for a total of 47 different products. In the case of permanent coatings, the graffiti is typically removed using some form of chemical or high-pressure water. If chemicals are used, they are applied to the graffiti and washed off with water.

Sacrificial coatings are generally coatings that use a wax material to coat any number variety of different surfaces.

When a surface has been painted, both the graffiti and the wax are removed using a variety of techniques. The wax coating would then be reapplied to the surface.

### ***Organic vs. Inorganic***

Twenty-seven of the products investigated were classified as organic coatings while information regarding the other products was unavailable. None of the coatings were classified as inorganic.

### ***Number of Coats***

Approximately 80 percent, 32 out of 41 of the permanent coatings provided information regarding the number of coatings that were required for their anti-graffiti setup. Of the products that mentioned how many coats were needed:

- One coat was recommended for 13 products,
- Two coats were recommended for another 13 products,
- Two to three coats were recommended for two products,
- Three coats were recommended for one product and
- More than three coats were recommended for three products. Nine products did not specify how many coats should be used.

### ***Cleaning Procedures***

Of the six sacrificial coatings, three suggest their own cleaner to be used along with a hot water blaster. Literature on one product was not available. The remaining sacrificial coatings required either a hot or cold water blaster.

Most of the permanent coatings recommended their own cleaning product to remove graffiti. Some of the companies recommended common citrus-based cleaners to be used along with hot water and a scrubbing tool, though in some cases, a pressure washer could also be used. Other products advised allowing time for the graffiti solvent to weaken the paint (about 5 - 30 minutes) before removing.

### ***Durability Studies***

Most of the products list durability as one of their products benefits; however, the definition of durability varies between each product. Only one product included an actual systematic durability studies study in their literature.

### ***DOT Field Demonstrations***

Review of published literature indicates that only 11 State transportation departments have had some form of interest in graffiti resistant coatings. Unfortunately, there are very few departments that have tried field demonstrations and therefore information on

their experience is very limited. Most evaluations of the products, from the reviewed published literature and web-searches, have been unfavorable.

### ***Self cleaning and De-Polluting Systems***

In addition to its graffiti resistant properties, the inorganic coating discussed in this report is also self cleaning and de-polluting. The components that comprise the coating are photocatalytic, that is, they are activated by ultra-violet light and act as a catalyst for the chemical reactions that lead to the self cleaning and de-pollution process. These particles, because they act only as catalysts, are not used up during the chemical reaction, therefore, continued use of the coating would not deplete or lessen the coatings ability to continue to function at the same rate.

Photocatalysis is the ability of a material to emit free-radicals upon exposure to UV radiation. These free-radicals are then able to oxidize organic substances such as harmful pollution. This area of study has received wide academic interest over the last three decades because of its potential to be used for pollution control in air and water. The most widely known photocatalysts are titanium dioxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), and cadmium sulfide ( $\text{CdS}$ ).

Titanium dioxide is found commonly in three different forms, namely, brookite, rutile, and anatase. Although rutile is the most common of the three, its photocatalytic ability is lower than that of the anatase phase which is also chemically stable and is not toxic. Brookite titanium dioxide, on the other hand, has no photocatalytic abilities.

Photocatalysis has been used to disinfect water by oxidizing the harmful organic chemicals into non-hazardous by-products. A similar process can be used to purify air pollutants such as nitrogen oxides ( $\text{NO}_x$ ), hydrocarbons and organic chlorides. Reactions in the atmosphere between  $\text{NO}_x$  and several hydrocarbons, in the atmosphere, under solar irradiation are known to create the condition referred to as "photochemical smog". Photochemical smog is, a mixture of chemicals and oxidants that have been linked to asthma, cardiac and pulmonary health effects within heavy traffic urban areas. In addition, sulfur oxides ( $\text{SO}_x$ ), formaldehyde, ammonia, chloroform, gasoline components, (e.g., benzene, and toluene), and tobacco smoke and have also been able to be neutralized by photocatalytic radiation. <sup>(5)</sup>

### **Durability of the Proposed Coating System**

The effectiveness and durability of the coating was evaluated previously using strength tests of flexural concrete prisms strengthened with carbon reinforcement and the inorganic polymer to be used for the coating. The tests were conducted before and after exposure to wet-dry and scaling conditions. Strengthening of prisms was done by

bonding carbon toes or fabrics to the tension side of the prisms using the inorganic polymer. This strengthened face was subjected to wet-dry and scaling conditions.

A more recent study, conducted under the sponsorship of NJDOT, led to the following conclusions which were based on more than 30 applications on walls, Jersey barriers and curbs on various campuses of Rutgers University: (These conclusions were based on more than 30 applications in walls and curbs on the Rutgers University campus and demonstration applications on New Jersey Barriers and walls near Douglass College.)

- The inorganic matrix coating can be applied to smooth or rough concrete surfaces with minimal surface preparation.
- Only excess dirt and standing water need to be removed before the application.
- The coating cures in 24-hours if the ambient temperature is more than 10° C.
- The coated surface has to be protected for 24-hours from direct rain or running water.
- Basalt, glass, and carbon fibers can be added to the matrix to improve the performance.
- Four different sets of application personnel were able to apply the coatings without any problems. Therefore, the field crew can be easily trained.

## **FIELD APPLICATIONS**

A total of three field applications were carried out to demonstrate the applicability, effectiveness, and long term performance of the proposed inorganic composite coating system. These projects were all completed in New Jersey and consist of: a retaining wall in South Orange, a retaining wall in Woodbridge, and a wing wall under an overpass in Milltown.

The first project was a retaining wall on Interstate 280, east of the Garden State Parkway overpass in South Orange, New Jersey. This project was the largest project attempted with a surface area of about 7,200 square feet and took 8 eight days to complete. The primary purposes of this project was were twofold: to demonstrate the coating's the ease of application of the coating and since this wall was located in an area with high concentration of graffiti, it could demonstrate and resistance to graffiti. resistant properties. This wall had a very uneven surface due to the precast concrete design simulating stone and mortar and it was located in an area with a high concentration of graffiti. In addition, a color scheme was developed to blend with the surrounding rock outcropping.

The second project was a retaining wall located on the east side of the northbound Route 1, near the west entrance ramp to at the Woodbridge Mall, ramp in Woodbridge, New Jersey. Access to the retaining wall was found by entering the west most parking lot at the Woodbridge Mall and continuing to the west side of the parking lot. In this project, a light grey color was used to match the existing color. This site was used to evaluate the self cleaning properties of the coating in on an actual structure.

The third project was on the east abutment of the Milltown Road over pass Bridge on Route 1 in Milltown, New Jersey. This location is often tagged with graffiti and is a major problem for the township and the NJDOT. The graffiti usually exhibits offensive language and gang related symbols, making cleaning a priority. This project, therefore, was to demonstrate the graffiti resistant properties of the coating and the ease of removal.

### **Color Schemes**

Prior to the application of the coating for the Route 280 and Route 1 sites, various color schemes were investigated.

Of the many different admixtures tested, iron oxide provides the best workability and color for red, yellow, and brown pigments. Chromium can be used to create brown and green tinted colors and yellow iron oxide works to form yellow tints.

### **Route 280 Retaining Wall Project**

The primary objective of this project was to demonstrated the viability of the new coating for on large transportation related surfaces encountered in transportation structures. The structure chosen was a retaining wall located at I-280 and Garden State Parkway in South Orange, New Jersey. The surface consisted of a pre-cast concrete with a surface area of about 7,200 square feet. The surface was in excellent condition and was pressure washed before the application of the coating in order to remove limited amount of dirt and possible precast form oil residue. The work schedule and the observations made during the execution of the coating procedure are described in the following sections.

### **Additives and Application Methods**

Additives were used in the coating in order to increase the pot-life. Pot-life is the period of time after mixing during which a resin remains suitable for use. If the coating is exposed to the sunlight for extended periods of time, a thin layer of skin forms over the top surface. It is not recommended that this skin be remixed into the liquid because it results in a lumpy and inconsistent finish. In warm temperatures, this skin will form quicker and in thicker layers. It was noted that by keeping the mixing tray in the shade,



this problem could be minimized. However, because the temperature midday climbed into the mid-80's to above 90° F, it was necessary to add increasing amounts of retarder, such as rubbing alcohol, to the mixture. After the rubbing alcohol was added to the mixture and then painted on the wall, the alcohol would be evaporated into the air as the coating cured.

While painting the Route 1 and Route 280 retaining walls, several different application techniques were used to apply the coating. Originally, a foam roller was used in order to increase the application area and decrease application time. However, it was found that the rubbing alcohol used to extend the pot-life of the coating would dissolve in the foam roller. In addition, the roller didn't conform to the rough surface leaving uncoated spaces. As a consequence, brushes and cloth rollers were used.

### **Color**

Initially, a gray shade was specified for the coating color. However, the coating color was modified using pigments to obtain a brownish color to blend with the shale next to the retaining wall. Trial patches were prepared at Rutgers Livingston lab. The shade of the color was varied to provide a realistic clay brick wall look appearance.

Based on the results of the coatings formulated at the lab, a brown color was found to best match the shale found at the site. A small amount of green dye was used with a large amount of red dye to create the optimal brown shade range. These polymer dyes accounted for less than 1 percent of the total weight, so the effect of the polymer on the inorganic matrix was minimal. The match at close-up and at a distance is shown in Figure 1.

Figure 2 shows the difference between the parent concrete surface and the coated concrete.



Figure 1. a) Close-up and b) From a Distance



Figure 2. Contrast between Parent and Coated Surfaces

### **Details of Field Application**

The coating operation was started on August 12, 2008 and finished on August 22, 2008. The coating was applied by three to four persons workers over a period of approximately eight days. The following observations were made during the coating operation:

- Coating operation was started around 7:30 am each day and finished around 3 pm.
- When the temperature was below 85°F, a retarder was not required to extend the pot-life. When the temperature exceeded 85°F, a quantity of one to two percent by weight retarder was needed to increase the pot life.
- On the first day, there was a thunderstorm around 5 pm, which lasted for about 15 minutes. This did not cause any damage to the coatings.
- On the third day, a thunderstorm that occurred around 5 pm that was stronger than the first storm caused streaking on the last panel that was coated at around 2:30 pm. This is consistent with the earlier observation that the coating should be protected against direct water contact for a period of three hours. Addition of retarder to compensate for the high temperature during the application also contributed to a delay in curing.
- The application rate was about 200 square feet per person worker per day. Since the wall is about 12 feet tall at some locations, part of the coating was applied using a ladder.
- The coverage was about 15 square feet per pound.
- Application was carried out using brushes and rollers though brushes provided a more uniform coat and deeper penetration in the rough surface.
- A darker color was obtained either by a thick first coat or by applying two or more coats.

- The grooves were not coated and this provided a pleasing brick and mortar appearance.
- The persons workers who applied the coating were comfortable with the process and did not have any complaints even though they were not professional painters.

### **Summary**

Details of the field demonstration project show that the inorganic-polymer coating can be easily applied to large surfaces. The system is easy to work with and the applications can be carried out using paint rollers or brushes.

Extensive surface preparations are not needed prior to the application of the coating except to have the surface pressure washed and allowed to dry.

Observations of the coating surface when magnified 200 times show uniform coverage and absence of cracking (as shown in Figure 3).

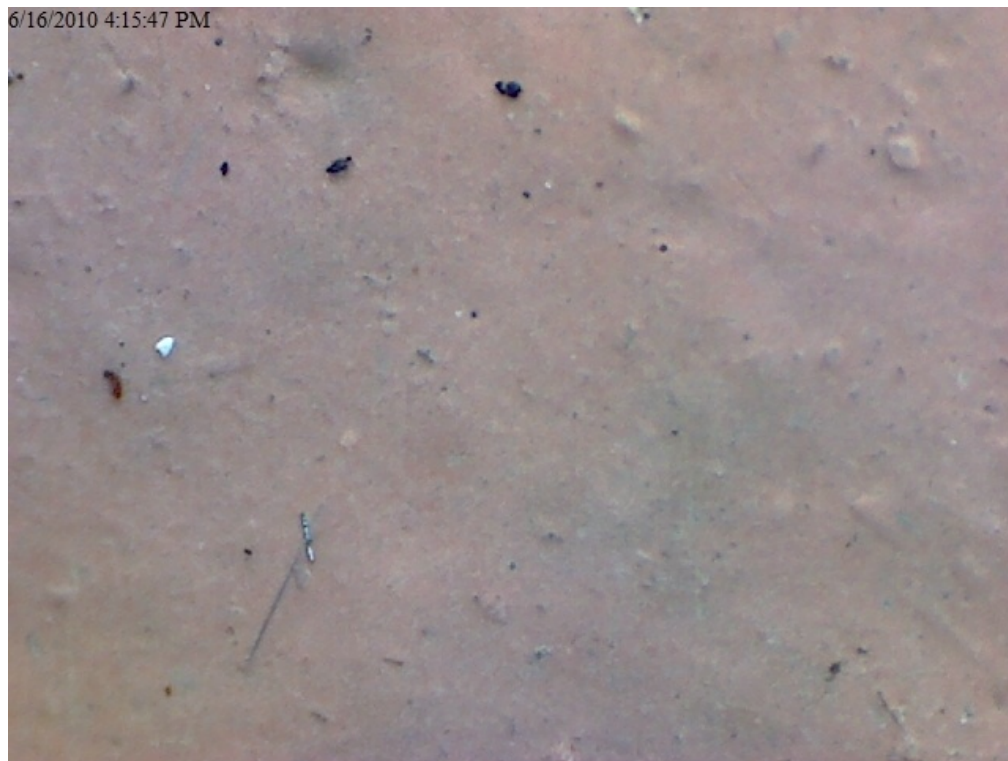


Figure 3. 200x Magnification of Coating Surface

Finished surfaces provide an aesthetically pleasing appearance as shown in Figure 4. An observation of the site after two years in operation indicates very good compatibility with parent material and resistance to deterioration (as shown in Figure 5).



Figure 4. Condition After Coating



Figure 5. Condition after 1 - 2 Years

### **Woodbridge Mall Retaining Wall - Route 1**

The primary objectives of this project site were to demonstrate the durability of the new coating for relatively large surfaces encountered in transportation structures and to measure the self-cleaning properties. The retaining wall chosen is located on the side of the exit ramp for the Woodbridge Mall off of Route 1 and is adjacent to the west most parking lot at the Woodbridge Mall. The coated surface consisted of rough pre-cast panels with a surface area of about 600 square feet. The surface was pressure washed before the application of the coating. The self-cleaning properties of the coating were determined quantitatively at this site and can be found in the Self Cleaning Properties section of this report.

### **Color**

This mixture features a balanced amount of red and green dye yielding a gray tint to match the actual new concrete color as seen in Figure 6.

### **Application**

The Rutgers team consisted of two people and was supervised by Dr. Balaguru. The retaining wall took approximately three days to coat. Preparation of the coating consisted of liquid and powder parts mixed in a high shear mixer along with the gray

pigment. The coating was applied using the same techniques developed in the I-280 retaining wall project location.



Figure 6. Detail of Coating

### **Summary**

The coating was applied using both rollers and brushes at this location. Brushes provide a little better texture coverage. The coating is performing well for more than a year (as shown in Figure 7 and Figure 8).



Figure 7. Condition after Application



Figure 8. Condition after 1 Year

## Milltown Abutment – Route 1

The primary scope of this project demonstrated how the coating provided a graffiti resistant surface and the ease of graffiti removal on small panels of the east Milltown Road bridge abutment at Route 1 in Milltown. The area being coated was constantly being tagged by graffiti thus providing the optimal testing ground for graffiti resistance and removal methods as shown in Figure 9. The existing concrete surface was several years old and stained from pollution, weather, and minor deterioration. The coated panels will also act to test and demonstrated the ability of the inorganic matrix in slowing down spalling and overall weakening of the concrete structure from age.



Figure 9. Graffiti at the Milltown Site

## Application

The application of the coating took a couple of hours to complete with two people. Several rectangular sections were coated on both sides of the bridge abutment (as shown in Figure 10). The color scheme used was taken from the similar to the I-280 Project location because of its aesthetic value and known qualities.





Figure 10. Coated Milltown Bridge Abutment

### **Summary**

As expected, the coating was quickly covered in graffiti after it was applied. The bridge crew responded by painting the abutment to cover the coating and graffiti. However, upon a return visit to check the condition of the coating, both the graffiti and cover paint were easily removed by scrapping the surface with a fingernail or pocket knife. The paint actually peeled off in small  $\frac{1}{4}$  to  $\frac{1}{2}$  inch sections (as shown insee Figure 11).



Figure 11. Demonstration of Paint Removal

## **EVALUATION OF GRAFFITI REMOVAL METHODS**

Due to the prevalence of graffiti on public structures, dozens of different products exist to attempt to clean the graffiti. These materials range from citrus-based graffiti removers to graffiti resistant coatings. The citrus-based strippers are usually sprayed on the graffiti and allowed to dissolve the paint and weaken the bond to the surface. Once the paint bond is weakened, the graffiti is either washed off with water or in some cases allowed to evaporate.

The available graffiti resistant coatings require either a power washer or hot water to remove the graffiti and in some cases the company has formulated its own graffiti removal product to use on their particular coating. The graffiti resistant coatings can be either a sacrificial coating that is removed along with the graffiti or a permanent coating. All of the coatings currently on the market are organic based, meaning that the chemical composition is carbon-based and therefore subject to natural deterioration. In contrast, the inorganic coating developed by Rutgers University is the only permanent inorganic coating in existence today allowing it to behave similar to concrete.

Three tests were developed to determine the most effective removal method for the inorganic coating. These three methods are hot water removal, citrus solution removal, and removal using a power pressure washer. Each of these three methods yielded positive results. The hot water removal would create a thin layer of water in between the paint and the surface and the paint would simply peel off. The citrus remover would be applied to the surface and allowed to penetrate the paint for a minimum of ten minutes and then be washed off with the graffiti. The pressure washer method easily removed the paint by holding the nozzle about six inches from the surface while moving the water stream in a sweeping motion overlapping the previous pass slightly.

### **Coating Types Summary**

Typical techniques used for removing graffiti are:

- Chemical and pressure wash
- Hot water
- Abrasives and water under pressure

For the inorganic polymer coating, the following techniques were evaluated:

1. Citrus chemicals with cold water
2. Citrus chemicals plus pressure washer with cold water
3. Hot water
4. Pressure wash with cold water
5. Pressure wash with hot water
6. Baking soda plus pressure washer

Citrus based solvents and abrasive baking soda were chosen for the graffiti removal testing trials because they are both approved for indoor use, are environmentally friendly, and are relatively inexpensive. Baking soda was used for an abrasive based on the same reasons.

## **Laboratory Results**

### **Citrus Solution and Cold Water**

In this method of graffiti removal, a citrus based solution, available at a local home improvement or hardware stores, and cold/lukewarm water were used. The supplies needed for this test were water, the citrus based cleaner, and a sponge. In this experiment, the letters "R U" were sprayed on the inorganic coating with a black spray paint. The "R" was removed using the citrus based solvent and water. The citrus cleaner is available in spray cans or in liquid form. The steps for removal are as follows:

Step 1: Mark the desired area for graffiti removal and collect all supplies.

Step 2: Spray or apply the citrus-based solution over the graffiti. Wait for about 20 minutes (minimum 10 minutes) before removal. With the sponge, remove the graffiti and citrus based solution. In this case, the graffiti was almost entirely removed with one swipe of the sponge, though to completely clean the surface, some extra wiping is required.

Step 3: Once the surface has been sufficiently scrubbed, use water to completely remove them the residual spray paint and citrus based solution from the surface.

Figure 12 shows the initial and end result. As can be seen, the "R" has been completely removed from the surface. This graffiti removal procedure took approximately 25 minutes from applying the solvent to the final rinse.



Figure 12. Before and After

### **Hot Water**

The next graffiti removal experiment involved the use of only hot water and a sponge.

The steps for removal are as follows:

Step 1: Mark the desired area for graffiti removal and collect the supplies that will be used for removal. This experiment will remove the “U” from the same exhibit that featured the spray painted “R U” letters.

Step 2: Using the sponge, apply the hot water to the area marked with graffiti. Although the hot water took a little more work to remove the spray paint than the citrus cleaner, it wasn’t difficult to entirely remove the “U” and entirely came off the coating coated surface.

Figure 13 shows the end result of removing graffiti using hot water and a sponge. As can be shown in Figure 13, the “U” had been completely removed using hot water and a sponge. The duration of this is experimental removal method was one and a half hours.



Figure 13. Before and After

### **Cold Water Power Washer and Citrus Solution**

This test used two coated pieces of plywood (the boards were two feet high by four feet long). One board was coated with the Woodbridge Mall retaining wall Route 1 coating and the other board by the shale color used for the I-280 site. In addition, two different spray paints were used to see if there was any difference in the removal process between the different paints. The steps required followed for removal are as follows:

- Step 1: Spread citrus solution on the graffiti. . In this demonstration, only the inside halves of each panel were covered with citrus solvent.
- Step 2: Allow 10 minutes (preferably 20 minutes) in between the application of citrus solution and cleaning of the graffiti with the power washer.
- Step 3: Run the power washer with the nozzle about six inches from the surface for the amount of time needed to effectively remove all of the graffiti. The power washer used had a pressure of 3000 psi.

Since the left part of the first “U” did not have any solvent applied, it can be seen that the use of the citrus cleaner greatly helps in graffiti removal because of the slight outline of the remaining paint (as shown in Figure 14). The use of a power washer using cold water did remove a small amount of the graffiti but not enough to be efficient. The total amount of time it took to remove the graffiti with the power washer plus the citrus solvent was a minute and a half after the equipment is set up. It should also be noted that this time would be faster where the parent surface is concrete instead of plywood.



Figure 14. Before and After

**Hot Water Power Washer**

The next graffiti removal experiment involved hot water and a power washer. This graffiti removal test was unsuccessful; therefore the steps used are not included.

As can be seen from Figure 15, the graffiti did not come off very easily. The pressure washer stream was applied for about 30 seconds with a nozzle range of 0 to 6 inches without any change in removal rate.



Figure 15. Before and After

### **Hot Water Power Washer and Citrus Solution**

The next graffiti removal experiment involved the use of a hot water power washer as well as citrus solution. It was shown earlier that the solvent works well by itself but to eliminate a mechanical scrubber and to have a method that works in hard to reach places, the pressure washer is used while connected to a hot water source. This combination is more successful than when the pressure washer is used alone. The steps followed for removal were as follows:

Step 1: Apply the citrus solution.

Step 2: Connect the power washer to the hot water and spray the affected areas.

In this demonstration, the graffiti was removed almost immediately by the power washer. Figure 16 shows the coating before and after it's been cleaned. As can be seen the hot water power washer and citrus solution method left a small outline of the sprayed "R" but otherwise did an excellent job removing the graffiti.

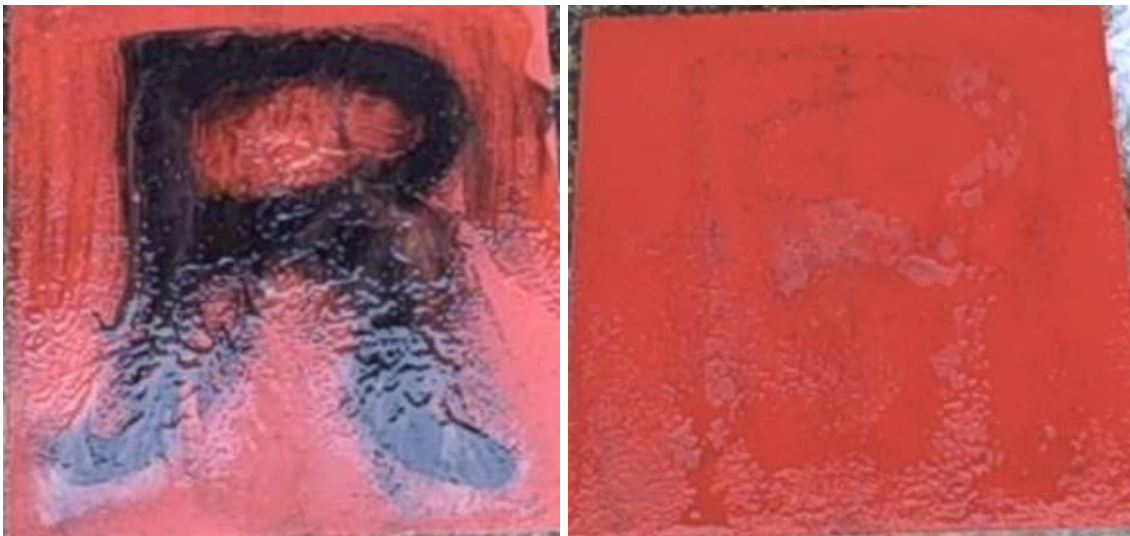


Figure 16. Before and After

### **Use of Baking Soda (Abrasive) with Hot Water**

The next graffiti removal experiment utilized a special pressure washer called the WADU Soluble Media Injector, distributed by Norton Sandblasting Equipment, to remove the graffiti. The WADU was connected to a regular pressure washer and acted like a sand blaster except that the abrasive was a baking soda product manufactured by Arm & Hammer called ARMEX. This experiment was also successful. The steps followed for removal were as follows:

Step 1: Connect the hot water to the power washer, the power washer hose to the WADU, and turn the WADU knobs to flow.

Step 2: Turn on the power washer and apply the ARMEX mixture to the desired area with the wand.

In just a few seconds, almost all of the graffiti was removed as shown in Figure 17. In just a few seconds almost all of the graffiti was removed. Although a small light shadow remains in some parts, the WADU did an excellent job of removing the graffiti quickly and with little effort. The residual shadow light shade that appears on the picture disappeared after a couple of days.



Figure 17. Before and After

## **SELF CLEANING PROPERTIES**

It is well known that the air is contaminated by fossil fuel pollution. Dust and mold from natural processes are also carried in the air. These soiling particles make their way to the concrete and steel structures. Then soiling agents corrode steel and deteriorate concrete surfaces. If the surfaces can be kept clean, long term durability of the structures can be improved in addition to enhanced aesthetics.

The inorganic coating used in the current investigation is photocatalytic, meaning when one of the components of the inorganic matrix, specifically potassium alumina-silicate, is activated, the coating self-cleans the corrosive pollution and prevents or slows down the above-mentioned deterioration mechanisms. Many of the soiling agents responsible for the deterioration of concrete are unable to adhere to the surface of this inorganic coating and then are neutralized or carried away by natural processes such as UV radiation and rainwater.



## **State-Of-The-Art**

At the CIB World Building Congress in 2004, the European project, named “Photocatalytic Innovative Coverings Applications for Depollution Assessment or PICADA”, put forth a research report on the development of a new self-cleaning self cleaning and depolluting material. <sup>(6)</sup> The self-cleaning self cleaning properties of this material were measured by monitoring the photocatalytic decomposition of an organic dye called rhodamin B.

Rhodamin B has an anthracene moiety and because of that is placed in the category of polycyclic aromatic hydrocarbon or (PAH)s. In other words, the rhodamin B dye is very similar to those soiling agents that cause the degradation of structures that can lead to structural failure in the future. The rhodamin B dye can be placed on a surface and the change in color can be recorded over time with a colorimeter. So the self-cleaning properties of the coating decompose the spot causing the color to fade. In their laboratory the PICADA team placed concrete samples one meter from a UV light to correspond with a desired 3700 Lux intensity. This intensity was chosen to limit the direct photocatalysis of rhodamin B and simultaneously allows photocatalytic decomposition to continue.

## **Test Setup**

Self -cleaning tests were conducted both in the lab and in out-door environments. Specimens tested outside were either at the Livingston lab using both artificial UV light and sunlight or at the Route 1 site near Woodbridge Mall using sunlight.

## **Indoor Tests**

The indoor rhodamin B tests utilized a UV light set-up and plywood coated with the inorganic coating. One of the sheets had titanium dioxide ( $\text{TiO}_2$ ) added into the mixture while the other plank had the regular inorganic coating applied to it (as shown in Figure 18 Figure 18).  $\text{TiO}_2$  is also a photocatalyst that is currently in use as a depollutant and will be used as a comparison to the unaltered coating. These boards were placed under a UV light and then four small red dots of rhodamin B were placed on the boards. Measurements were then taken with the colorimeter at 0, 1, 2, 4, 8, 12, 24, 36, and 48 hour increments. Samples one and two are on the  $\text{TiO}_2$  side and samples three and four were placed on the side coated with the regular mix.



Figure 18. (a) Setup for Rhodamin B Tests (b) Rhodamin B Dot

### **Outdoor Tests**

The outdoor rhodamin B tests utilized a natural sunlight and the same plywood setup as the indoor tests. Two sets of tests were run conducted outdoors. The first set of tests had a 48-hour test run duration outside the Rutgers lab and the second set of tests were done over a one month period at the Route 1 (Woodbridge Mall) site and again outside the Rutgers lab.

The first set of tests consisted of a piece of plywood placed in the sunlight. Half of this plywood sheet was coated with the coating plus  $\text{TiO}_2$  and the other half was the regular mix. Measurements were then taken at 0, 1, 2, 4, 24, and 48 hours increments. Fewer tests were done for the 48-hour outdoor test than for the 24-hour indoor tests because the reading had to be taken during daylight hours.

The second set of tests were conducted by placing a series of eighteen dots on the retaining wall at the Route 1 (Woodbridge Mall) site. These dots were then measured with the colorimeter at 0, 1, and 24 hours, 7 days and finally 1 month increments.

### **Test Results**

#### **48-Hour Test Results - Indoor**

In samples one and two (with  $\text{TiO}_2$ ), approximately 74 and 68 percent respectively of the dye was decomposed within a 24 hour period. Samples three and four contained the inorganic coating without any  $\text{TiO}_2$  added and they recovered approximately 72 and 89 percent of their original color within the first 24 hours. The difference between the samples with  $\text{TiO}_2$  and those without are negligible, thereby verifying the effectiveness of the stand-alone coating for this test as seen in Figure 19.

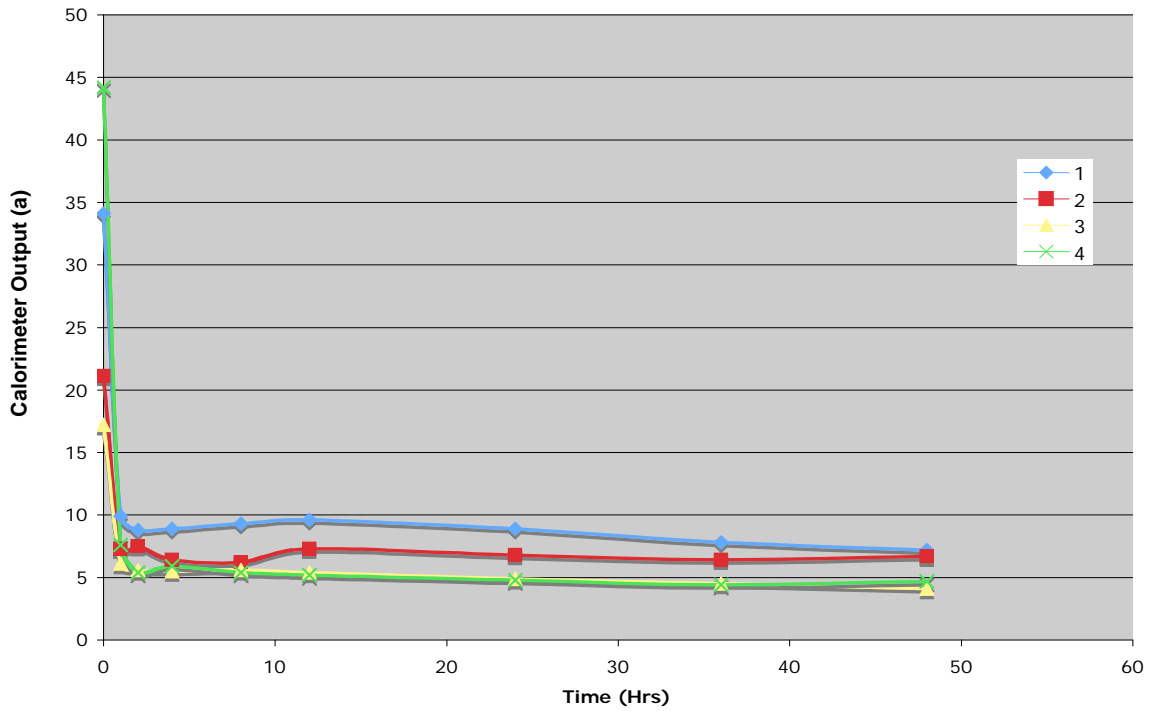


Figure 19. 48-Hour Indoor Tests

**48-Hour Test Results - Outdoor**

This test was done in a similar manner to the indoor tests: four spots of the dye, distributed evenly over the TiO<sub>2</sub> side and the regular side. Also the findings were similar to the indoor tests in that the original color was almost entirely recovered over the test period for all four test samples without any difference made between the TiO<sub>2</sub> and regular coating mix (as shown in Figure 20).

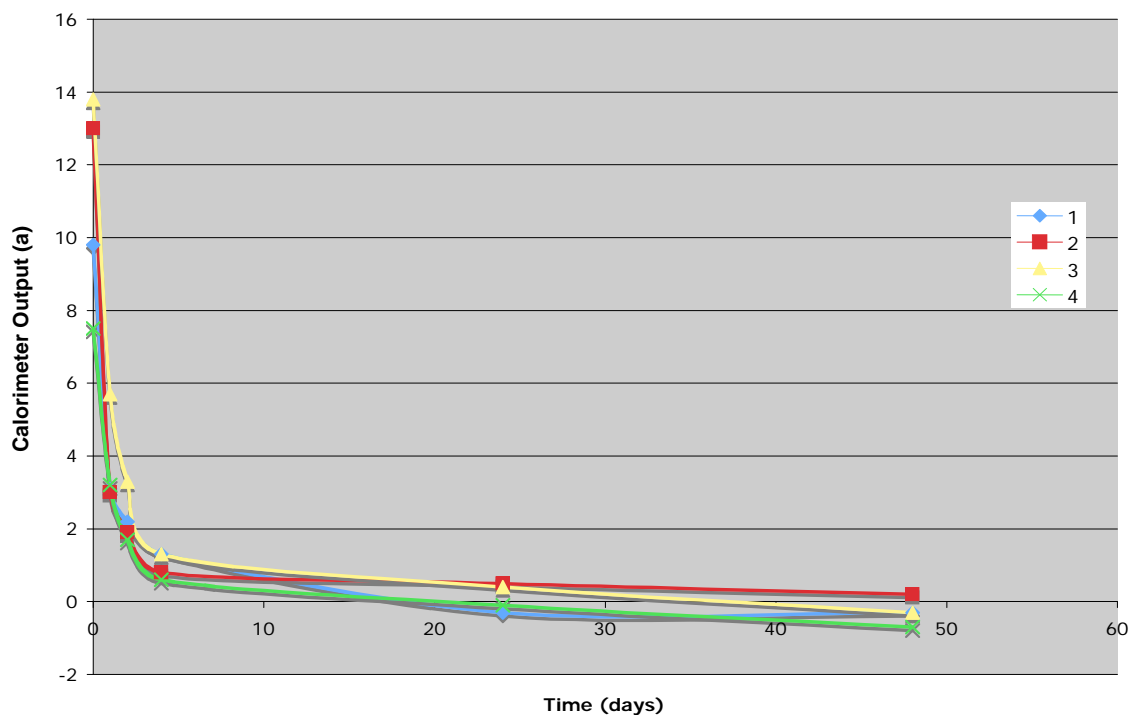


Figure 20. 48-Hour Outdoor Tests

### Livingston Lab Results

Figure 21 shows the color change of seven samples of different colors due to the degradation of the rhodamin B dye over a two-month period. These various samples contained different mix proportions in addition to different types of dying agents. None of these samples contained  $\text{TiO}_2$ . These 7 seven samples recovered approximately 43, 28, 82, 84, 93, 94, and 98 percent respectively of their original color within a 2 two-month period.

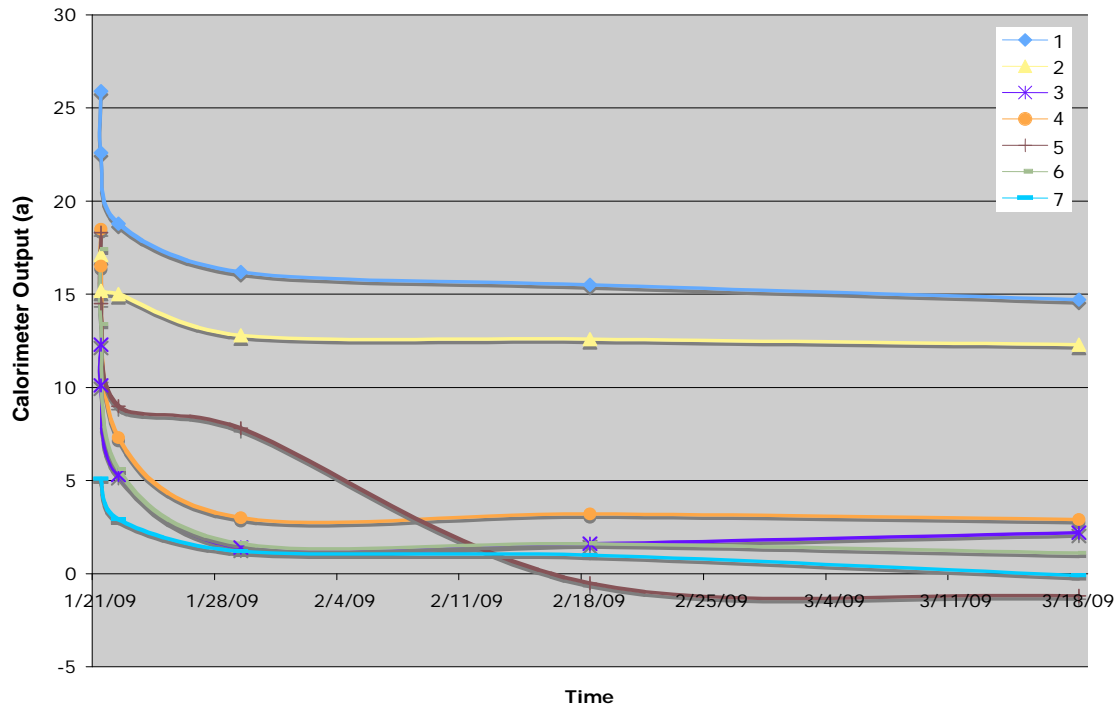


Figure 21. Livingston Lab Test Results

### **Woodbridge Mall Retaining Wall - Route 1 Results**

The outdoor test results were monitored over a one-month period. The rhodamine B dye had to be used in a higher concentration in these tests in order to get high enough values for an accurate analysis of the dye destruction. In order to quickly find the five dots for future readings a blue permanent marker was used to trace the edge of each dot. However, at the seven day reading, the dye had virtually disappeared and at the end of the one-month period both the permanent marker and dots were extremely difficult to find as indicated by in Figure 22.

All of the dots that were monitored on the wall were in places where only one layer of the coating had been applied. Attempts were made to apply the dye to sections of the wall that had been given two coats but the dye did not stick to the coated surface because the surface was so too smooth and the dye would simply run off the wall as shown in(see Figure 23).

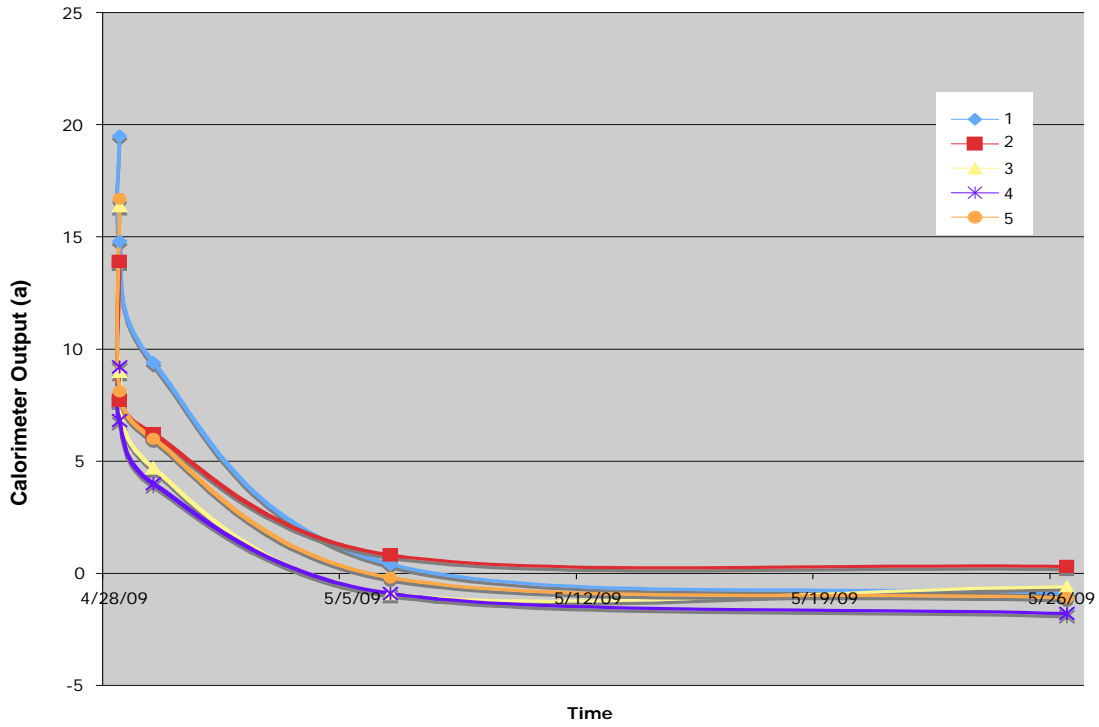


Figure 22. Woodbridge Mall Retaining Wall - Route 1 Test Results

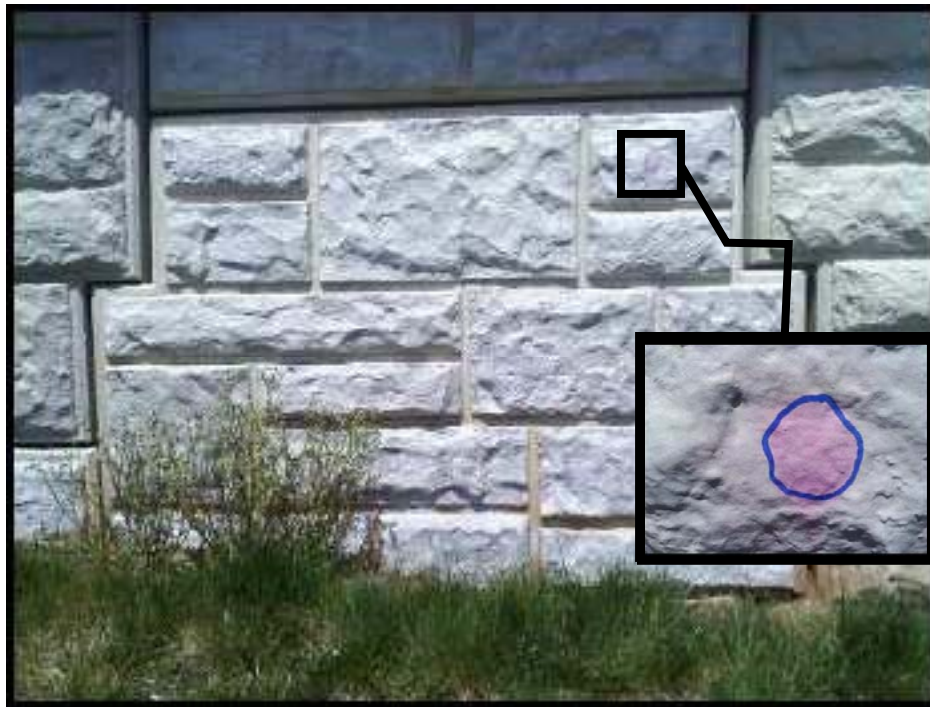


Figure 23. Woodbridge Mall Retaining Wall - Route 1 Wall with Rhodamin B Dot

## EVALUATION OF DEPOLLUTING CHARACTERISTICS

As cars burn fossil fuels, many volatile organic compounds or (VOCs) as well as mono-nitrogen oxide or  $\text{NO}_x$  particles are released into the environment. The nitrogen cycle reduces most unstable or harmful forms of  $\text{NO}_x$  into stable  $\text{NO}_x$  forms. For example, nitrogen dioxide, which is a volatile gas, can be reduced to nitrate or nitric oxide which, in turn, can be reduced to the harmless and beneficial nitric acid and nitrous oxide. However, nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) can be very harmful to the atmosphere and to human beings. This section deals with the evaluation of the effectiveness of the inorganic coating for conversion of nitric oxide and nitrogen dioxide into more stable gases in the nitrogen cycle and in so doing to reduce the pollution in the air which results in a reduction of air pollution.

### State-of-the-Art

As mentioned earlier, the European project, PICADA, introduced a report on the development of a new self-cleaning and depolluting material. This material would have several different functions including increasing of the life cycle of buildings, self cleaning cement and other surfaces, and depolluting the air by utilizing a special process called photocatalysis. In short, photocatalysis is the process by which a chemical reaction is accelerated by the presence of light energy, in this case, ultraviolet (UV) light.

Titanium dioxide, when exposed to UV light, acts as a photocatalyst for the decomposition of organic molecules adsorbed or occluded on its surface. The mechanisms involved in removing volatile gases from the air are not simple. It is assumed that nitric oxide (NO) in the air is oxidized when the  $\text{TiO}_2$  is exposed to UV light. The result of this oxidation is nitrogen dioxide, which is in turn converted to nitrate. While some of the NO and  $\text{NO}_2$  particles may escape into the air from the photocatalytic surface, most particles that come in contact with the surface will be effectively trapped together in the resultant nitrate salt.<sup>(7)</sup> This new material was engineered as a binder for cement-based materials and organic-based coatings. Its effectiveness as a depollutant of volatile organic compounds (VOC's) and nitrogen oxides is typically increased in canyon type street settings where pollutants are generally trapped between high walls.

The uses of these photocatalytic materials are numerous. According to estimates from the American Lung Association, one out of every three members of the US population lives in an area with unhealthy levels of ozone. Harmful ozone is comprised mainly of nitrogen oxides and VOC's that most photocatalytic cements can reduce by between 20 to 80 percent. Researchers at Essroc Italcementi Group, Marco Barbesta and Dan Schaffer, have estimated that in Milan, Italy, where air quality standards sometimes force local administrators to shut down automobile traffic for a full day at a time, could become 50 percent cleaner if just 15 percent of the buildings and roads were resurfaced with photocatalytic cement products.<sup>(8)</sup> Due to the low costs of these materials and

their extensive benefits, for both the environment and the life times cycles of infrastructure, many new applications for photocatalytic self cleaning and de-polluting materials have been researched over the past few years. In 2003, over 800 international patent applications were published for photocatalytic materials.

In the same article, Barbesta and Schaffer describe the current applications, availability, and uses of self cleaning and depolluting cements currently on the market or in some stage of the development process. Photocatalytic cement can be used for sound barriers, concrete pavers, blocks and facade elements. The article also outlines several of the environmental aspects of cementitious photocatalytic materials. For example, the final products of the reactions in the de-pollution process include quantities of nitrates and sulfates that studies have shown to be of negligible quantities that do not contribute significantly to soil and ground water nitrification.

Recently, the Italcementi Group has patented a new self cleaning cement product called TX Active. This product is one of the many self cleaning and de-polluting compounds that removes both nitrogen oxides and VOC's from the air. This newly patented product can be used as a cement or plaster that helps save improve the environment and reduces maintenance costs. In addition to the TX Active, which is available in gray and white colors and comes in Portland cement type I, II, and III, Italcementi's TX Aria adds de-polluting properties to the self cleaning properties. Several structures have been built in the United States using such materials to reduce cleaning costs. For example, a white precast concrete carillon tower was constructed in Dalton State College in Georgia. There is an area lin Hyacinth Place (a "green" housing project in Highland Park, Illinois), that is constructed out of concrete pavers made with photocatalytic cement. Photocatalytic cement was also recently used to create 2 -two 30 foot tall gateway elements at the entrances to the new I-35W bridge in Minneapolis, MN.

## **Mechanism**

One of the most important properties of the anatase form of titanium dioxide is the energy band gap. The energy band gap is an energy range in a solid where no electron state exists. In other words, it is the distance that exists in between the valence band and the conduction band of a solid that an electron must jump over to occupy one of those bands. The larger the band gap, the more difficult it is for a valence electron to jump to the conduction band or valence band. It is an important property in condensed matter physics.

When a photon has enough energy to match or exceed the band gap energy, an electron is promoted from the valence band into the conduction band leaving a void. In this excited state, one of three things can happen:



1. The first case is that the conduction-band electron can recombine with the valence-band void and dissipate the input energy as heat.
2. In the second case, the conduction-band electron and valence-band void can get trapped in a meta-stable surface state.
3. In the third case, the conduction-band electron and the valence-band hole can react with electron donors and electron acceptors absorbed on the solids surface or within the surrounding electrical double layer of the charged particle.

The concept of an electron band gap is useful in understanding the interaction of light with matter. The size of the band gap relates inversely to the amount of light that can be absorbed by the material. This means that a larger band gap will absorb light in the short wavelength UV region while a small band gap will absorb light in the high wavelength visible range.

The band gaps of the anatase and rutile forms of titanium dioxide are 3.02 and 3.23 eV, respectively. A band gap of less than four electron volts is defined as a semiconductor. Semiconductors, such as zinc oxide (ZnO), iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ), cadmium sulfide (CdS), zinc sulfide (ZnS), and titanium oxide ( $\text{TiO}_2$ ) can act as sensitizers for light induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band.

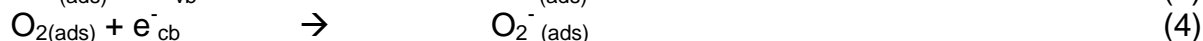
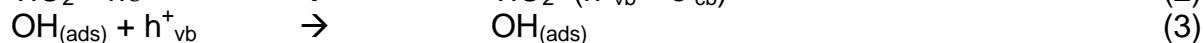
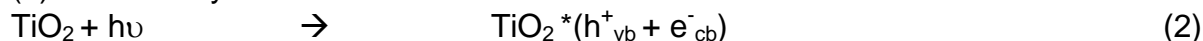
Primary steps in the photo-electrochemical mechanism are:

1. Formation of charge carriers by a photon
2. Charge carrier recombination to liberate heat
3. Initiation of an oxidative pathway by a valence-band hole
4. Initiation of a reductive pathway by a conduction-band electron
5. Further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products
6. Trapping of a conduction band electron in a dangling surficial bond to yield Ti (III)
7. Trapping of a valence-band hole at a surficial titanol group

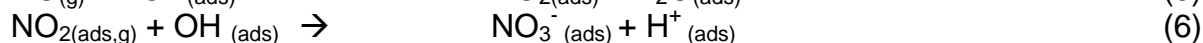
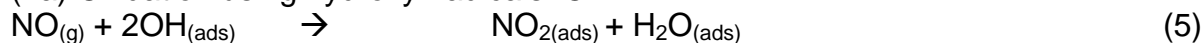
When the conduction-band electron and the valence-band hole reacts with electron donors and electron acceptors absorbed on the solids surface such as NO, the resultant

chemicals are generally non-toxic. For example, nitrates are a very common transformation product for photocatalysis of NO. In addition, nitrates are not harmful to the environment since they are easily consumed and recycled by plants. <sup>(9)</sup> The level of nitrates converted from NO increases with the photocatalytic activity of the material. Pollutants such as NO and NO<sub>2</sub> produce HNO<sub>3</sub> when completely oxidized. In addition to nitrates, a small part of the NO is converted into N<sub>2</sub>O upon desorption. The process of NO and NO<sub>2</sub> oxidizing to HNO<sub>3</sub> is shown below:

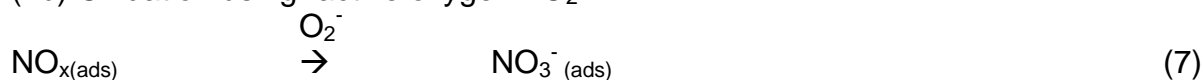
(1) Photocatalysis



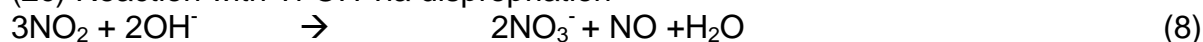
(2a) Oxidation using hydroxyl radicals: OH



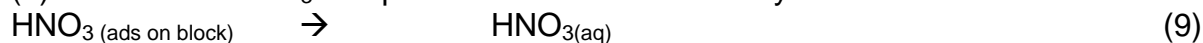
(2b) Oxidation using “active oxygen”: O<sub>2</sub><sup>-</sup>



(2c) Reaction with Ti-OH via disproportionation



(3) Removal of HNO<sub>3</sub> complex from surface of block by water



## Air Purification

As harmful substances continue to pollute the air we breathe, it is important to attempt to clean the air. The use of titanium dioxide in pavement, concrete, and paint mixes is a viable option to accomplish this. The use of titanium dioxide reduces not only NO<sub>x</sub> gases but also VOC's such as benzene, toluene, ethyl-benzene, o-xylene, aldehydes, and carbonals carbonyls to create clean air. When exposed to sunlight, the titanium dioxide transforms these volatile gases into non-toxic compounds.

Outdoor pollutant concentrations typically are in the low parts per million (ppm) ranges. Studies have shown that because of the easy dispersion of volatile gases in an open environment, de-pollution is most effective in canyon streets. In a recent study, researchers set up TiO<sub>2</sub>-mortar panels 5.2 meters high with a gap of 2 meters in between the panels and then introduced NO<sub>x</sub> gases into the setup. The variables of this experiment were pollution source emission, wind direction, and the orientation of the wall. The reduction in NO<sub>x</sub> gases was between 40 – 80 percent when compared to a reference canyon street setup that contained ordinary panels. <sup>(10)</sup>

## **NO Absorption of TiO<sub>2</sub>**

NO is an important molecule from the point of view of its environmental impact as a component of NO<sub>x</sub> from motor vehicle emissions. First principle calculations based on density functional theory have been performed to determine the binding configuration and the binding energy for NO on the TiO<sub>2</sub> single crystal surface. The most stable configuration is a tilted one, with the NO molecules bound to surface Ti sites as Ti-NO species. The calculated binding energy of the NO molecule is 43.7 KJ/mole at one-half the saturation coverage. <sup>(11)</sup>

While most of the NO desorbs without reaction, above a critical NO coverage a small part of the NO produces N<sub>2</sub>O upon desorption. As the N<sub>2</sub>O begins to be produced at higher coverage, there is an associated decrease in the NO yield. It is likely that the onset of NO dimer formation, predicted in the density functional calculations at high coverage, is associated with the N<sub>2</sub>O product. <sup>(12)</sup>

## **Reaction Variables**

There are many variables that will increase or decrease the efficiency of the photocatalytic reaction of titanium dioxide other than the form of titanium dioxide used. These variables include:

- Semiconductor concentration
- Reactive surface area
- Porosity of aggregates
- Concentration of electron donors and acceptors
- Incident light intensity
- pH
- Presence of competitive sorbates
- Temperature

## **Effect of UV-Light Intensity**

Semiconductors, such as titanium dioxide, can absorb just enough sunlight (wavelengths between 300 and 365 nm) to have sufficient energy to overcome the band gap between the valence and conduction bands. The band gap size of titanium oxide only absorbs UV light. As the intensity of the UV light increases, more energy is absorbed by the surface to create valence-band holes and conduction-band electrons,

which in turn react with the volatile gases in the surrounding air. This means that as the UV light intensity increases, the energy absorbed by the titanium dioxide molecules will also increase resulting in a higher level of photocatalysis, de-pollution and cleaner air.

## **Research Program**

The aim of the de-pollution research reported documented in this thesis report is to evaluate the reduction of NO and NO<sub>2</sub> particles by the inorganic coating in a closed environment. The self-cleaning self cleaning inorganic matrix has zinc oxide, ZnO, as one of the constituent materials. For the purpose of de-pollution, TiO<sub>2</sub> was also added to the inorganic coating. Several recent studies have shown that the anatase form of titanium dioxide is the most active compound for reducing the amount of volatile gases in the air.

These studies This demonstration project have added several other particles to see whether or not the added particles enhanced the ability of the compound. Variables in this study include the differences in reduction levels of NO and NO<sub>2</sub> gases based upon their exposure to UV light or sunlight, the initial concentration levels of NO and NO<sub>2</sub>, and the presence of ZnO combined with TiO<sub>2</sub> or the presence of ZnO alone.

## **Test Setup**

A special test set-up was fabricated for the current study as shown in Figure 24. An air tight transparent polyethylene bag was fabricated in which various concentrations of NO and NO<sub>2</sub> were placed. In this each bag, a plywood samples coated with the composite were was placed to study the effectiveness of the coating. Half of the samples have had TiO<sub>2</sub> added in to the mixture. The NO<sub>x</sub> concentration is then monitored using a sensor. This project required the same test to be conducted inside as well as outside to observe the differences in NO and NO<sub>2</sub> reduction from a UV light versus the UV rays of sunlight. As soon as the gas is was put into the bag, the testing began.



Figure 24: . Setup for Indoor De-pollution Tests Results

## Results

### Indoor Test Results

#### ***Nitric Oxide Reduction***

The tests were conducted at with two concentrations of nitric oxide (NO): 30 ppm and 60 ppm.

The indoor NO tests were done a total of three times in two trials. For the first half hour of measurement of both the 30 ppm and the 60 ppm NO concentration tests, there was virtually no reduction in gas concentration at all. The trials where ZnO was the only de-polluting agent showed a more gradual reduction in NO gas while the trials with TiO<sub>2</sub> combined with the ZnO had a steeper reduction in NO towards the end of the trials test duration. Overall the trials test with TiO<sub>2</sub>, the higher concentration of NO gas, that is the 60 ppm, showed a slightly higher level of de-pollution reduction for trials both with and without TiO<sub>2</sub>, although the difference was minimal.

The test results showed a positive reduction of the 30 ppm NO gas as shown in Figure 25. The addition of TiO<sub>2</sub> to the coating showed an average 43.5 percent reduction concentration in the 30 ppm NO gas over after a 6 six hour period duration. The inorganic coating itself showed an average of 47 percent reduction in 30 ppm NO gas over after a six hour period duration. Slightly better than when used with TiO<sub>2</sub> as seen in Figure 25.

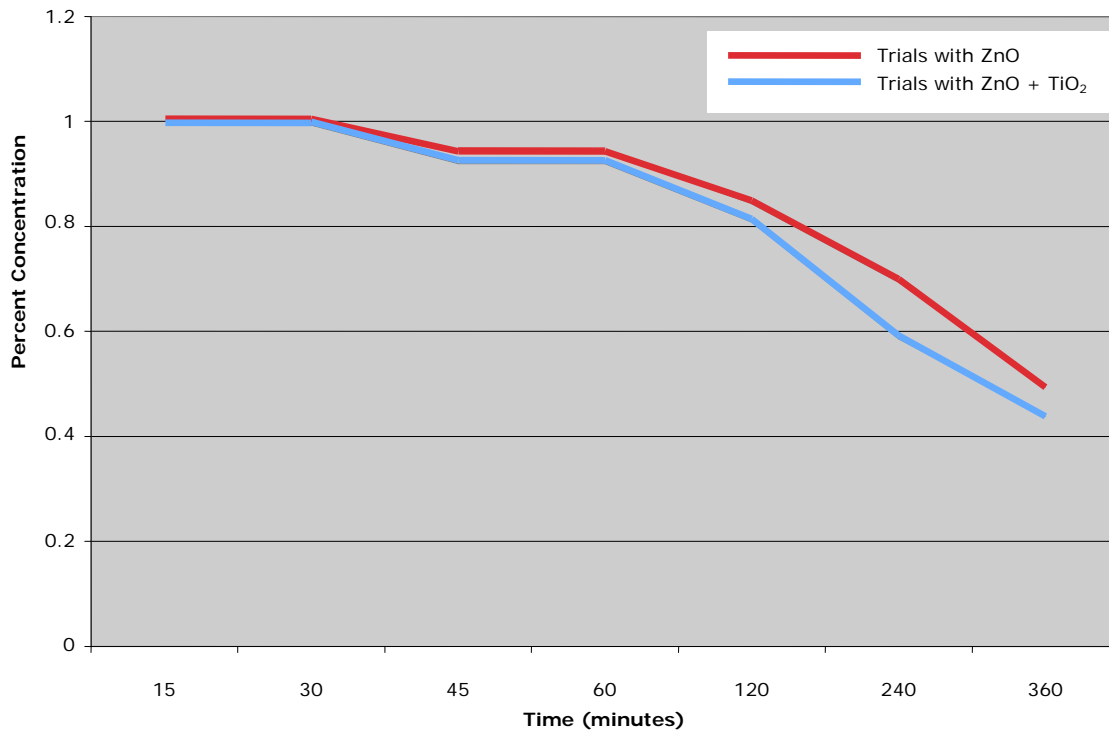


Figure 25. 30 ppm Nitric Oxide Reduction without Titanium Dioxide Gas Concentration (Indoor)

The results of the sixty ppm nitric oxide gas test was used in these test are shown in Figure 26, and produced the following results. In order to keep the results analogous to previous tests, these tests were conducted over a six hour period even though it would have taken longer than that to eliminate all nitric oxide from the bag. After a six hour test period, the percent reduction of those trials that included TiO<sub>2</sub> in the coating had an average of 45 percent concentration of 60 ppm NO gas while those trials that did not contain TiO<sub>2</sub> were had an average of 39.7 percent concentration of 60 ppm NO gas, this time slightly lower than if TiO<sub>2</sub> were present (see Figure 26).

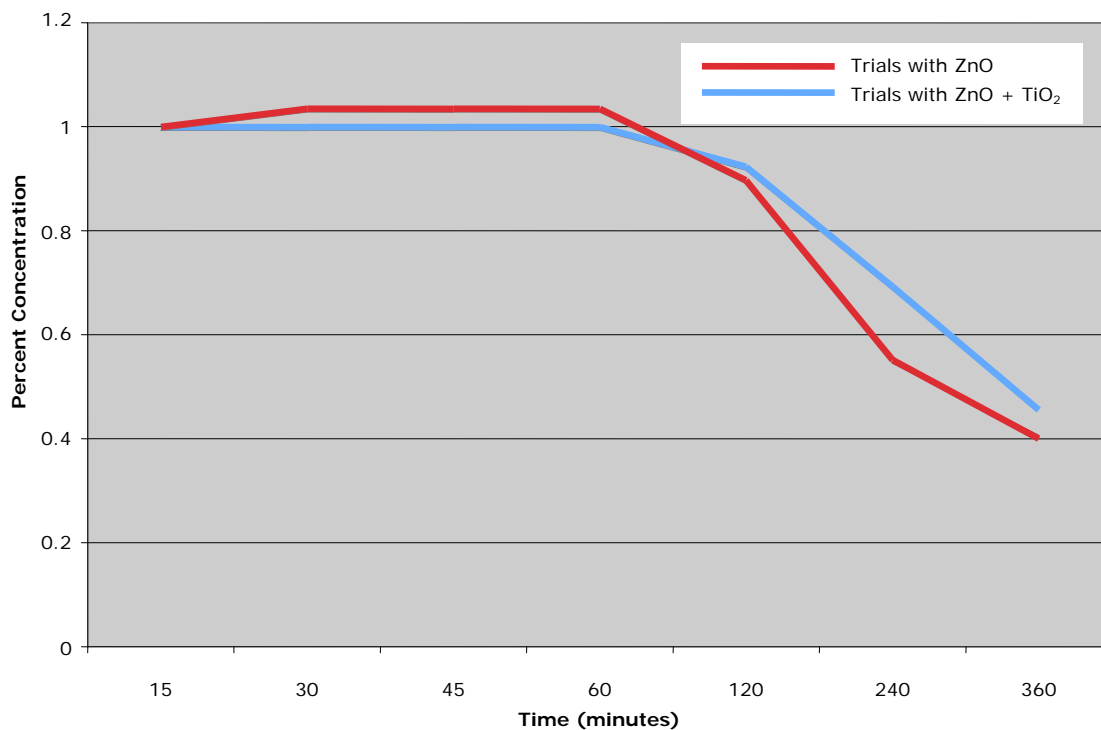


Figure 26. 60 ppm Nitric Oxide Gas Concentration with Titanium Dioxide (Indoor)

### ***Nitrogen Dioxide Reduction***

The indoor NO<sub>2</sub> de-pollution tests were performed in three trials plus a control trial. In addition to these tests an additional test A control trial was run without any de-pollution agent coated sample where the NO<sub>2</sub> sensor was placed inside the bag that was then filled with NO<sub>2</sub> gas. This was done to determine if there were problems with the test setup that might be affecting the interpretation of the actual de-pollution results. The percent reduction without any sample in the gas was slight but not enough to account for the reduction that is was caused by the coating.

After 45 minutes, the NO<sub>2</sub> was almost completely reduced by the trials with the coated samples, both with and without TiO<sub>2</sub>, while the NO indoor tests had reduced nearly 60 percent of the original amount of NO after 6 hours. This shows that while the coating does a very good job of reducing the amount of NO in the air, it does an even better job of reducing NO<sub>2</sub>. In these tests, it can also be seen that again the presence of TiO<sub>2</sub> did not have a major significant advantage on the reduction of the NO<sub>2</sub> gas. It is interesting to note that the coating with just ZnO took the same amount of time for a complete reduction of the NO<sub>2</sub> gas whether the initial concentration was 30 ppm or 60 ppm NO<sub>2</sub>.

The 30 ppm NO<sub>2</sub> test results, shown in Figure 27, showed positive improvement in the reduction of the NO<sub>2</sub> gas. The addition of TiO<sub>2</sub> showed an average 97.7 percent reduction in concentration of 2.3 percent of the 30 ppm NO<sub>2</sub> gas after a 45 minute period test duration, whereas the two trials with just ZnO had no detectable percent concentration of the 30 ppm (it is noted that in two of the tests absolutely no NO<sub>2</sub> gas was detected after the test period).

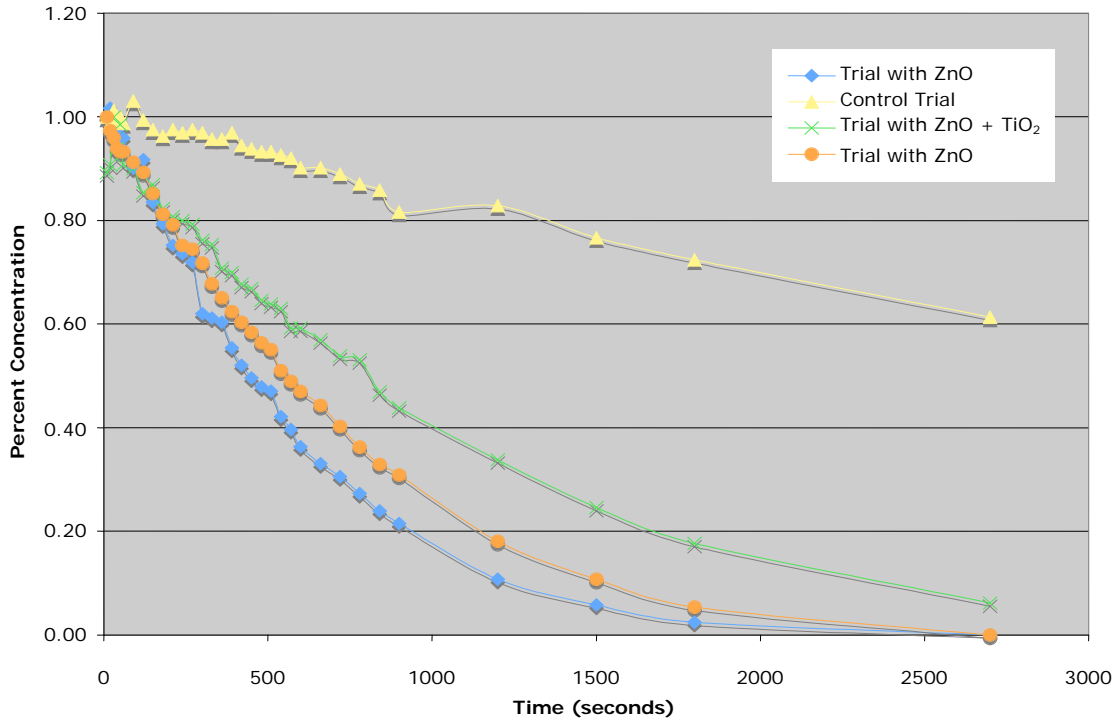


Figure 27. Nitrogen Dioxide 30 ppm NO<sub>2</sub> Gas Concentration Reduction with Titanium Dioxide (Indoor)

The 60 ppm NO<sub>2</sub> test results, shown in Figure 28, the inorganic coating itself showed an average 98.3 concentration of 1.7 percent reduction of the 60 ppm NO<sub>2</sub> gas after a 45 minute period test duration. Similarly, the two trials with just ZnO had no detectable percent concentration of the 60 ppm NO<sub>2</sub> gas after the test period. The 100 percent reductions would indicate that as the initial concentration increases the amount of time it takes to completely eliminate all NO<sub>2</sub> also increases.



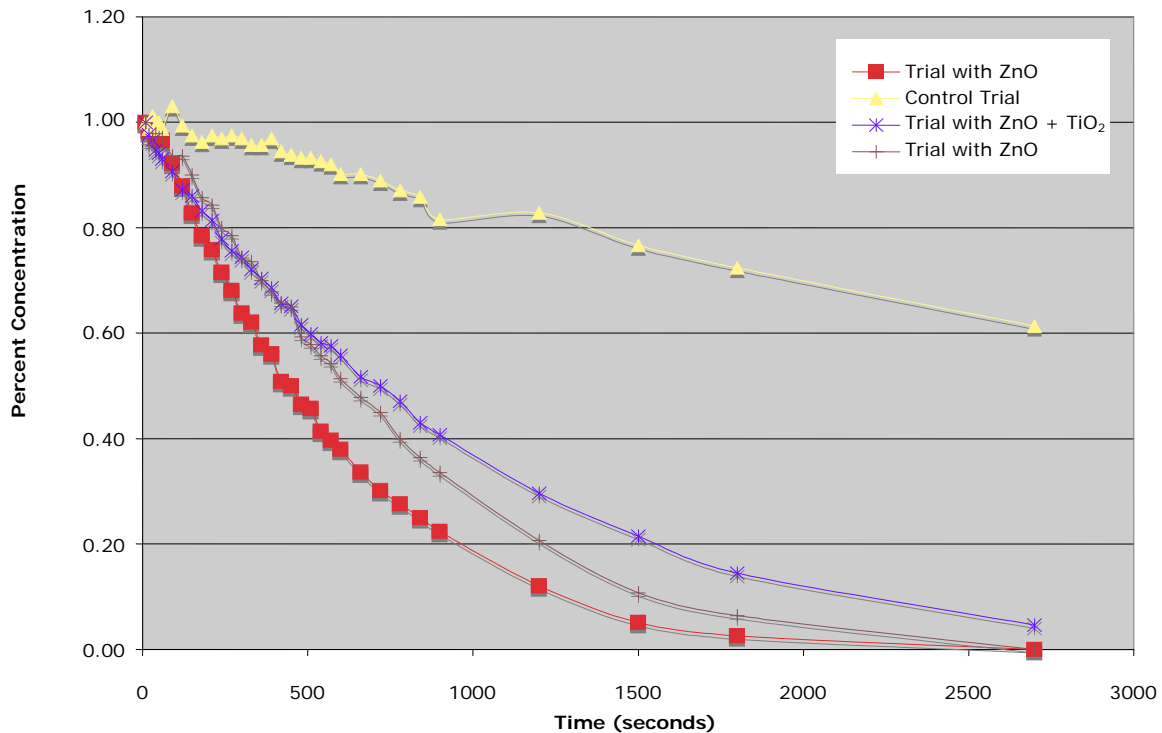


Figure 28. Nitrogen Dioxide Reduction without Titanium Dioxide 60 ppm NO<sub>2</sub> Gas Concentration (Indoor)

The indoor 60 ppm NO<sub>2</sub> depollution tests were also done a total of three times. After the 45-minute test an average of 1.8 percent of the original amount was left in the bag for all tests, with and without TiO<sub>2</sub>. This The test results demonstrates that the coating is very effective at reducing the amount of NO<sub>2</sub> in the air. As a side note, recall that NO<sub>2</sub> has two conversion processes. One converts NO<sub>2</sub> into HNO<sub>3</sub> and the other converts NO<sub>2</sub> into NO and oxygen. Since NO is still a pollutant, it was also monitored in the NO<sub>2</sub> tests. However, the NO quantities generated during these tests but though the tests created small quantities of NO though these quantities never rose above a six ppm level.

Finally, an average reduction of 97.6 percent in NO<sub>2</sub> gas over a 45 minute period was reached for those tests which used TiO<sub>2</sub>. In addition, an average 98.6 percent reduction in NO<sub>2</sub> gas was found for those tests which did not include the use of TiO<sub>2</sub> (see Figure 27 and Figure 28).

## **Outdoor Test Results**

### ***Nitric Oxide Reduction***

The outside tests were conducted from approximately 10 am to 4 pm where the temperature range was between 70°F and 80°F. Three Two outdoor tests were performed with Nitric Oxide (NO), one with a 30 ppm NO and the other with a 60 ppm NO concentration. Each test had two trials, one done with the regular inorganic mix coating containing ZnO and another three tests were done with the inorganic mix coating containing ZnO, plus TiO<sub>2</sub>.

The results in Figure 29 and Figure 30 of both outdoor NO tests show a drastic reduction in the amount of NO, regardless of which coating trial was measured, in both the TiO<sub>2</sub> and regular coating setup between two and four hours into the test. During the first two hours of the test, there was virtually no reduction at all. The last two hours was similar, with very little reduction. It is observed that the middle two hours of the test would always occur around noon to 2 pm at which point the sun is highest in the sky, the temperature is highest throughout the day and the energy in the ultraviolet (UV) rays from the sun is also highest. This means that during these two hours the TiO<sub>2</sub> coatings received UV rays that were high enough to activate the ZnO and TiO<sub>2</sub> photocatalysts and in so doing caused very high levels of NO reduction. However, during the last two hours of the test the TiO<sub>2</sub> and inorganic coating particles seem to have deactivated due to a reduction in the magnitude of the sun's UV rays.

The test results showed a positive improvement in the reduction of the 30 ppm NO gas as shown in Figure 29. The samples with the addition of TiO<sub>2</sub> showed an average concentration of 30 ppm NO gas of 8.391.7 percent after the 6 hour period test duration. Similarly, the inorganic coating itself showed an average concentration of the 30 ppm NO gas of 84.315.7 percent reduction in NO<sub>2</sub> gas overafter the 6 hour period test duration.

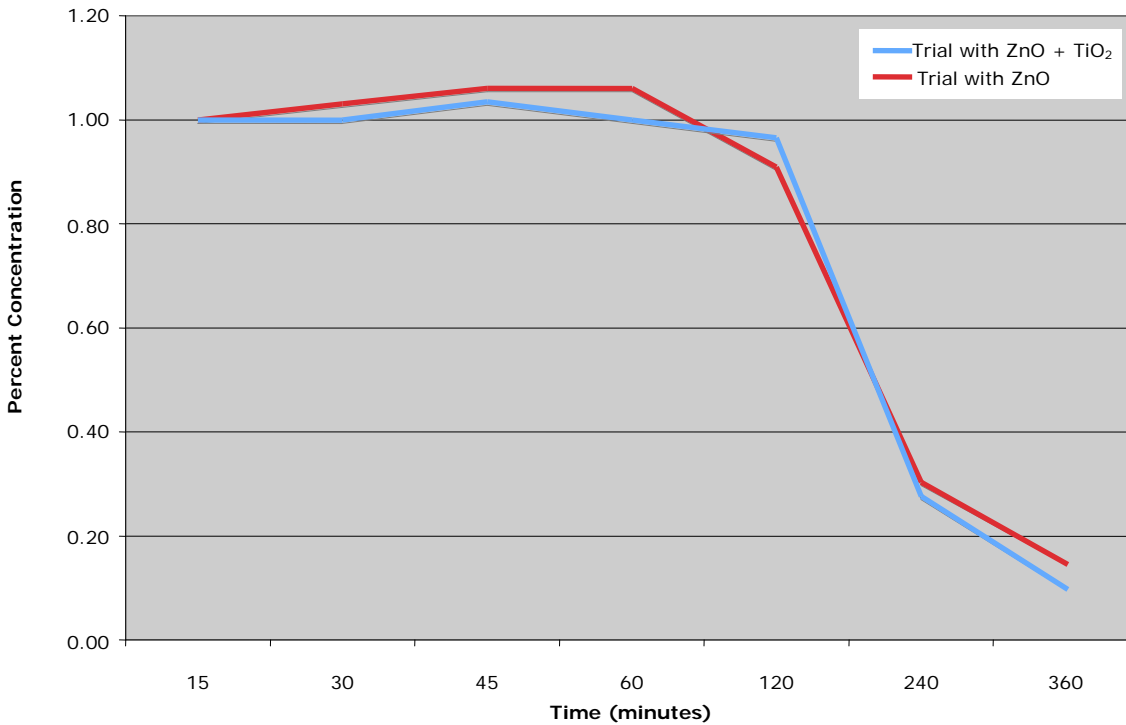


Figure 29. 30 ppm Nitric Oxide NO Gas Concentration Reduction with Titanium Dioxide (Outdoor)

The next nitric oxide tests was completed with a concentration of 60 ppm of NO gas. In order to keep the results analogous to previous tests, this tests were conducted over a 6 hour period even though it would have taken longer than that to eliminate all nitric oxide from the bag. Over After athe 6 hour period duration, the percent reduction concentration of 60 ppm NO gas remaining for the trials that contained TiO<sub>2</sub> was an average 76.723.3 percent while those trials that did not contain TiO<sub>2</sub> had an average of 71.328.7 percent, as shown in Figure 30.

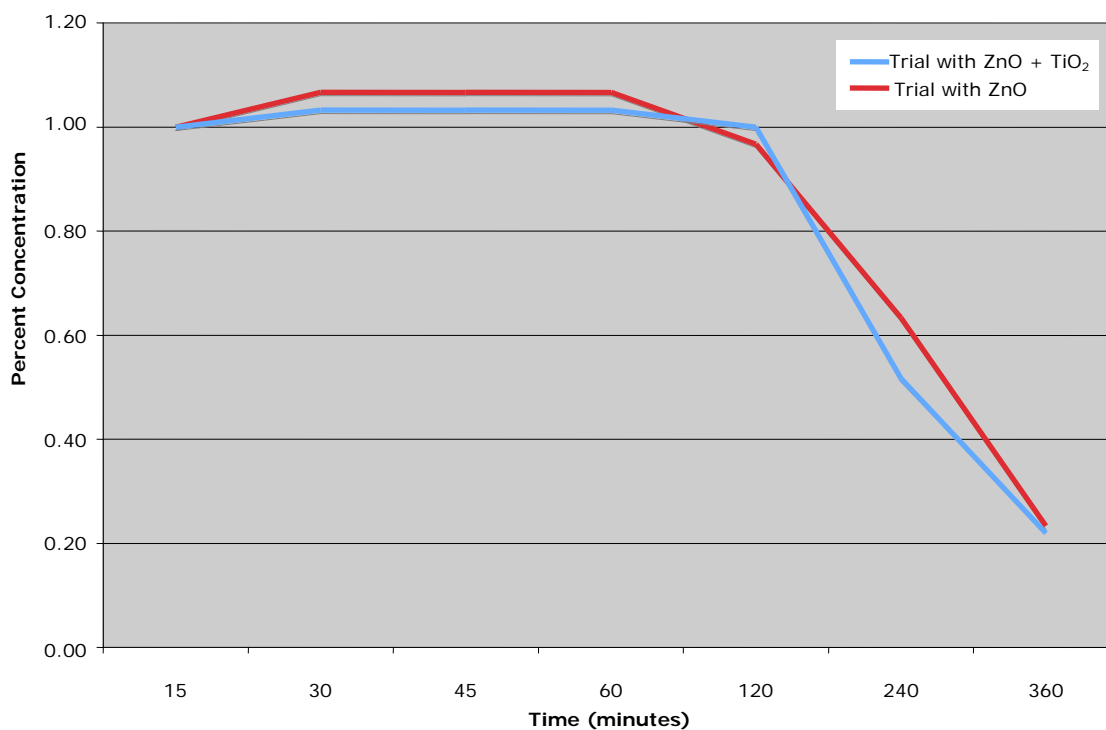


Figure 30. 60 ppm NO Gas Concentration Nitric Oxide Reduction without Titanium Dioxide (Outdoor)

### ***Nitrogen Dioxide Reduction***

The outdoor NO<sub>2</sub> depollution tests were done a total of three times. It took 45 minutes or less to complete the reduction of NO<sub>2</sub> gas. It may be noted that in some of the cases that did not include titanium dioxide, it only took 25 - 30 minutes to eliminate all of the NO<sub>2</sub>. Although the trials that did not include TiO<sub>2</sub> were more effective in the reduction of NO<sub>2</sub>, these trials did contain excess NO at the end of the 45 minutes and took longer to decompose the NO after decomposing the NO<sub>2</sub>. In comparison, the trials that did include TiO<sub>2</sub> took longer to reduce the concentration of NO<sub>2</sub> to zero but did so by converting the NO<sub>2</sub> particles to HNO<sub>3</sub> instead of NO.

These tests were started at 10 in the morning and finished around 3 in the afternoon. The three tests conducted without TiO<sub>2</sub> were done first followed by the three tests that did include TiO<sub>2</sub>. During the final tests, clouds blocked some of the sunlight. This resulted in a slightly slower reduction in NO<sub>2</sub> gas but in all cases All the outdoor NO<sub>2</sub> depollution tests of the ZnO coating, both with and without TiO<sub>2</sub>, resulted in zero percent concentration of the NO<sub>2</sub> gas by the end of the 45 minute test period. was completely reduced by the end of the experiment period.

As mentioned earlier, the nitrogen cycle converts the  $\text{NO}_2$  gas into  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{HNO}_3$ . During all trials shown in the graphs The sensors indicated, during the outdoor  $\text{NO}_2$  gas tests, that as the amount of  $\text{NO}_2$  was reduced, the level of  $\text{NO}$  increased. Despite this, the length of the test was kept to 45 minutes long even though it would have taken a lot longer to reduce the remaining nitric oxide ( $\text{NO}$ ) in the bag. It is interesting to note that the tests took the same amount of time to complete as those whose initial concentration was much lower.

### **UV versus Sunlight**

It was observed that the sunlight does a much better job activating the  $\text{ZnO}$  and  $\text{TiO}_2$  particles than UV light bulbs. The strength of the UV rays causes these particles to speed up the process of de-polluting the air. It should also be noted, however, that the increase in the efficiency of the inorganic coating with or without  $\text{TiO}_2$  occurs not throughout the entire day while the sun is out but only during certain times of the day when the sun's rays are high strong enough in magnitude. In New Jersey, this time is mostly between the hours of noon and 2 pm. However, depending on the latitude of the structure and the season, the amount of time when these depolluting particles are active throughout the day may vary.

The outdoor tests were more aggressive in their reduction of the  $\text{NO}$  gas. The outdoor tests have rates of reduction 30 percent higher than the indoor tests.

### **Presence of $\text{TiO}_2$**

The presence of  $\text{TiO}_2$  in the coating with  $\text{ZnO}$  appears to have little difference in the reduction of  $\text{NO}_2$  particles. Although the  $\text{NO}_2$  trials that contained just the  $\text{ZnO}$  coating  $\text{TiO}_2$  particles reduced the same level of  $\text{NO}_2$  particles in as much time as the samples with  $\text{TiO}_2$  within the 45 minute test duration, . the  $\text{ZnO}$  trials had a slightly higher rate of reduction than the trials with  $\text{TiO}_2$  that do not contain  $\text{TiO}_2$ , meaning that their rate of reduction is slightly higher. However, this difference is negligible since the concentration of  $\text{NO}$  particles increases where the concentration of  $\text{NO}_2$  particles decreases during those trials without  $\text{TiO}_2$ .

### **Initial Concentration of $\text{NO}$ and $\text{NO}_2$ gases**

The test results indicate a higher rate of reduction for the lower initial concentration tests. At the same time the final ppm reduction value was much higher for higher concentration tests. At times the reduction value for the 60 ppm tests was double that of the 30 ppm tests! This could mean that the higher the level of initial concentration the more particles come in contact with the coated surface and are then eliminated. Because the initial concentration was double in the 60 ppm case twice as many particles came in contact with the surface.

In almost every setup, the percent reduction was over 95 percent and over half the trials had a percent reduction of 100 percent. It is interesting to note that even though the initial concentration was doubled for half the trials it still took approximately 45 minutes to complete the tests. It occurred in only a small number of cases that the concentration of nitrogen dioxide was reduced to zero within a 25 - 30 minute period though it did happen even during a 60 ppm test. It can be seen that the indoor trials that contained an initial concentration of about 40 ppm, 30 ppm and 60 ppm in the samples containing TiO<sub>2</sub> were not able to completely reduce all of the NO<sub>2</sub> to zero over the 45-minute period. The graphs trends are very similar for the 30 ppm and 60 ppm tests.

## **CONCLUSIONS**

Based on the results reported in this investigation and observations made during the investigation and field applications, the following conclusions can be drawn.

### **Demonstration Projects**

A total of three field applications were carried out to demonstrate the applicability, effectiveness, and long term performance of the proposed coating system. These projects were all completed in New Jersey and consisted of : a retaining wall along I-280 in South Orange, a retaining wall off of Route 1 in Woodbridge, and an abutment along Route 1 in Milltown.

The I-280 project was a 7,200 square foot retaining wall near the Garden State Parkway. This project was the largest project and took eight days to complete. In part this project demonstrated the ease of application of the coating. The four person painting crew provided by the NJ DOT contractor was efficient and comfortable in coating the wall and there were no complications that prevented a successful completion of the project.

The second project was a retaining wall adjacent to the ramp going into the Woodbridge Mall on Route 1. This project used a light grey color and was meant to demonstrate the self cleaning properties of the coating. The application of the coating was completed over a two-day period. Once again there were no obstacles or surprises. AT two year assessment of the wall showed very positive results. The wall showed no sign of aging or discoloration. It has not been marked by graffiti and looks exactly as it did the day it was coated.

The third project was a bridge abutment in Milltown on Route 1. This location is often tagged with graffiti and is a major problem for the township. The coating was applied without any complications and when painted with graffiti, the graffiti was easily removed. The removal of graffiti was done with the help of NJDOT crew that provided traffic safety and water.

## **Graffiti Resistance**

To the best of the authors knowledge, the inorganic coating developed by Rutgers University is the only permanent inorganic coating available that can resist graffiti and be easily cleaned without specialized techniques and/or supplies. In order to compare it to the other graffiti resistant/remover products in existence, the same graffiti removal techniques used in practice were attempted to remove graffiti on the inorganic coating. These methods included removal with a cold water and citrus solution, hot water, citrus solution with a cold water pressure washer, citrus solution with a hot water power washer, a hot water power washer, and the soluble media washer (i.e. baking soda product with WADU Soluble Media Injector). Each of these tests yielded positive results with the exception of a the hot water power washer. However, when the hot water power washer was combined with the citrus solution, it worked perfectly.

## **Self Cleaning**

The inorganic coating being used in this research project is photocatalytic; that is, UV light from the sun activates the inorganic matrix to decompose harmful pollutants. Many soiling agents are unable to stick to the surface of the inorganic coating and end up being washed away by rainwater. This was seen throughout the tests as the soiling dye used was unable to stick to vertical surfaces and would end up beading and running down the wall, especially if the surface had two or more coats. The rhodamin B dye, due to its similarity to such soiling agents, was used to measure the efficiency of the inorganic coating's self cleaning properties. In both laboratory and field tests, the coating was able to clean itself of these soiling agents within a four-hour period even without any rain to wash away the soiling agents.

## **Depollution**

As cars burn fossil fuels many volatile organic compounds (VOC's), as well as  $\text{NO}_x$  particles, are released into the environment. Nitric oxide (NO), as well as nitrogen dioxide ( $\text{NO}_2$ ), are two forms of  $\text{NO}_x$  that can be very harmful to the atmosphere and to human beings.

Influence of  $\text{TiO}_2$  on the de-pollution efficiency of the inorganic coating was evaluated in this project. Variables in this project include the differences in reduction levels of NO and  $\text{NO}_2$  gases based upon their exposure to UV light or sunlight, the initial concentration levels of NO and  $\text{NO}_2$ , and the presence of ZnO combined with  $\text{TiO}_2$  or the presence of ZnO alone.

As expected, sunlight does a much better job of activating the inorganic matrix than the UV bulbs. The results clearly indicate that the outdoor tests were more aggressive in their reduction of NO and  $\text{NO}_2$  particles. In addition, during the middle of the day, between 12 to 2 pm, when the UV rays from the sun are strongest, the reduction in NO

particles took place at a much higher rate than at other times throughout the day. It was also noticed that it would take about an hour to get the inorganic matrix fully active in its reduction of NO gas. These two trends were not noticed observed in during the reduction of NO<sub>2</sub> tests. There appears to be no correlation between the reduction of NO<sub>2</sub> and the time of day or the amount of time the coating has been exposed to the light as depollution began immediately at a quick rate.

The presence of TiO<sub>2</sub> appears to have little difference in the reduction of nitric oxide particles.

Those trials that altered the initial concentration of NO gas show a higher rate of reduction for the lower initial concentration tests. At the same time the ppm reduction was much higher for higher concentration tests. This could mean that the higher the level of initial concentration, the more particles come in contact with the coated surface and are then eliminated. Because the initial concentration was double in the 60ppm case, twice as many particles came in contact with the surface, yielding a higher ppm reduction of NO particles.



## References

1. Balaguru, P. & Kurtz, S., *Repair and Rehabilitation of Reinforced Concrete Structures*, presented at Proceedings of the 1997 International Seminar on Repair and Rehabilitation of Reinforced Concrete Structures, Venezuela, 1997 (unpublished).
2. Balaguru, P., Nair, B., Rahimian, T. & Zhao, Q., Novel Geopolymer Based Composites with Enhanced Ductility. *Journal of Materials Science, Volume 42, Number 9*, 3131-3137 (May 2007).
3. Balaguru, P., Lyon, R. E. & Papakonstantinou, C. G., Comparative Study of High Temperature Composites. *Composites Engineering Part B, Volume 32, Issue 8*, 637-649 (December 2001).
4. Balaguru, P. & Foden, A., Properties of Fiber Reinforced Structural Lightweight Concrete. *Structural Journal, Volume 93*, 62-78 (January 1996).
5. Gokaraju, R. K., A Study on Anti-graffiti, Self-cleaning and De-polluting Coatings for Environmental Remediation.
6. Valee, F. . e. a., *Innovative Self-Cleaning and De-Polluting Facade Surfaces*, presented at CIB World Building Congress, Toronto, Canada, 2004 (unpublished).
7. Cassar, L., Photocatalysis of Cementitious Materials: Clean Buildings and Clean Air. *Materials Research Society, Volume 29, No. 5*, 328-331 (May 2004).
8. Barbesta, M. & Schaffer, D., Concrete that Cleans Itself and the Air. *Concrete International* (February 1, 2009).
9. Dalton, J. S. . e. a., Photocatalytic Oxidation of NO<sub>x</sub> Gases using TiO<sub>2</sub>: A Surface Spectroscopic Approach. *Environmental Pollution*, 415-422 (2002).
10. Maggos, T. . e. a., Photocatalytic Degradation of NO<sub>x</sub> in a Pilot Street Canyon Configuration using TiO<sub>2</sub> Mortar Panels. *Environ Monit Assess* (2008).
11. Yates, Jr., J. T., Solar Driven Photooxidation Chemistry on TiO<sub>2</sub> Surfaces for Environmental Cleanup (February 2001).
12. Balaguru, P. & Slattum, K., Test Methods for Durability of Polymeric Fibers in Concrete and UV Light Exposure. *ACI Special Publication, Volume 155*, 115-136 (1995).