

Photocatalytic Coating on Road Pavements/Structures for NO_x Abatement

Presented to

Houston Advanced Research Center

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Operating room



Photocatalysis is a Green Technology for Environmental Applications

Disinfection of Hospital Rooms (e.g., SARS viruses)

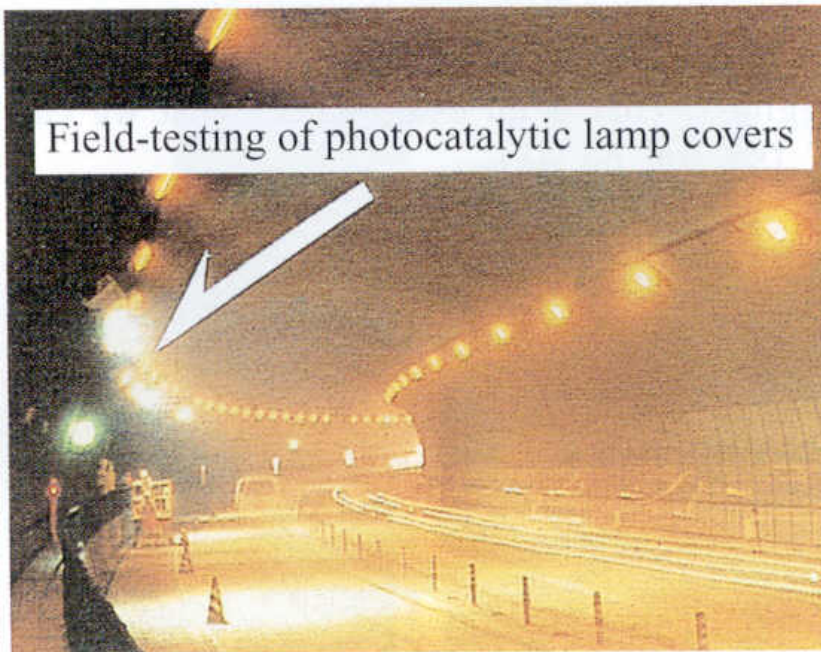


VOC oxidation into water, CO₂ and chlorides

- Indoor Air Cleaning
- Process Vent /Groundwater Treatment

(Courtesy of Mitsubishi Paper Mills , Ltd.)

Self-cleaning photocatalytic lamp covers use photocatalysis under fluorescent light to oxidize grease/soot in urban traffic tunnels.



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Nighttime and daytime processes of pollutant removal, and the regeneration of the TiO₂- photocatalyst (Koji Takeuchi, Institute for Environmental Management Technology, Japan).

a) Adsorption of air pollutants especially during the night	b) removal of air pollutants by oxidation during the day	c) regeneration of catalyst by rainfall during the day
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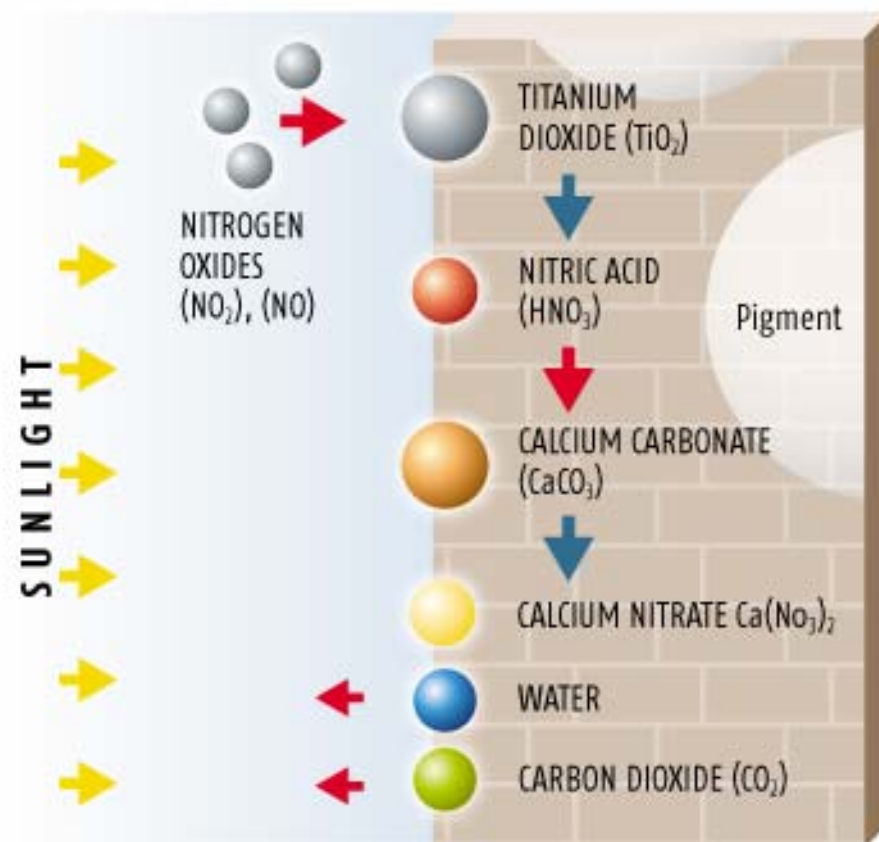
Pollutant-removal chemical reactions (courtesy of Hogan, New Scientist, February 2004)

PAINT REACTION

Capturing energy from sunlight to neutralise pollution

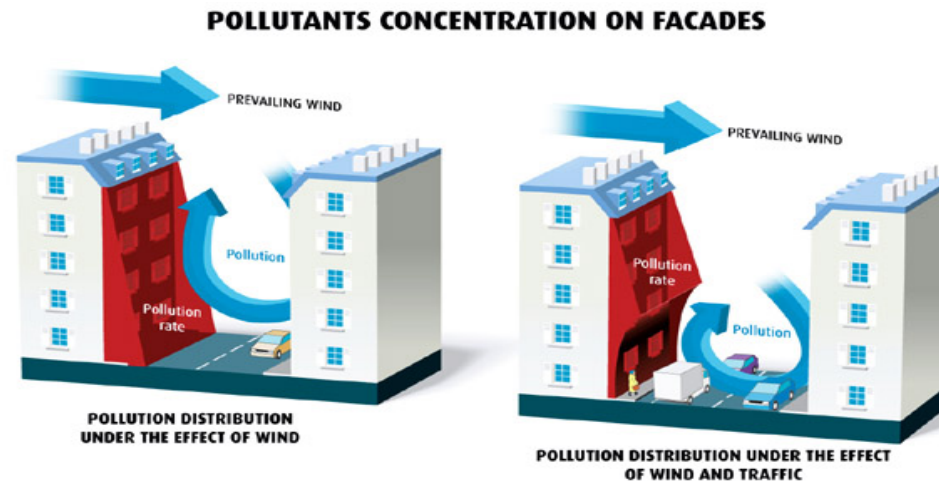
Titanium dioxide particles absorb energy from UV in sunlight. Nitrogen oxides adsorbed onto the particles are converted to nitric acid

The acid then reacts with calcium carbonate, locking the NO_x gases up in calcium nitrate, releasing CO₂ and water



European Experience

- In 2002, 7000 square meters of road surface in Milan, Italy, were covered with a catalytic cement
 - Residents reported that it was noticeably easier to breathe - with the concentration of nitrogen oxides at street level cut by up to 60 %.
- More recently, Westminster borough of London cooperated with Mitsubishi Materials Corporation to pave roads with TiO_2 - containing paving stone (NOXER)
 - Under an intensity of UV light of 12 W/m^2 , an 80% NO_x removal rate was achieved in the lab test (1 ppm NO_x ; the UV intensity of direct sunlight in summer is $20\text{-}30 \text{ W/m}^2$, compared to 1 W/m^2 on a cloudy winter day).
- Euro PICADA (Photocatalytic Innovative Coverings Applications for Depollution Assessment)
 - The 6-countries, 3.4 M€PICADA project is testing photocatalytic concrete streets and walls in urban areas.



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European Experience



TX Millennium brand (Italcementi Group)

In addition to pollution abatement, **photocatalytic white cement keeps architectural concrete clean and white (maintaining their aesthetic appearance unaltered in time)**

Japanese Experience

- The market for photocatalytic cements and paving slabs is growing
 - tested in Osaka, Chiba, Chigasaki & Saitama-Shintoshin
 - more than 50,000m² of such materials have been installed in Japan.



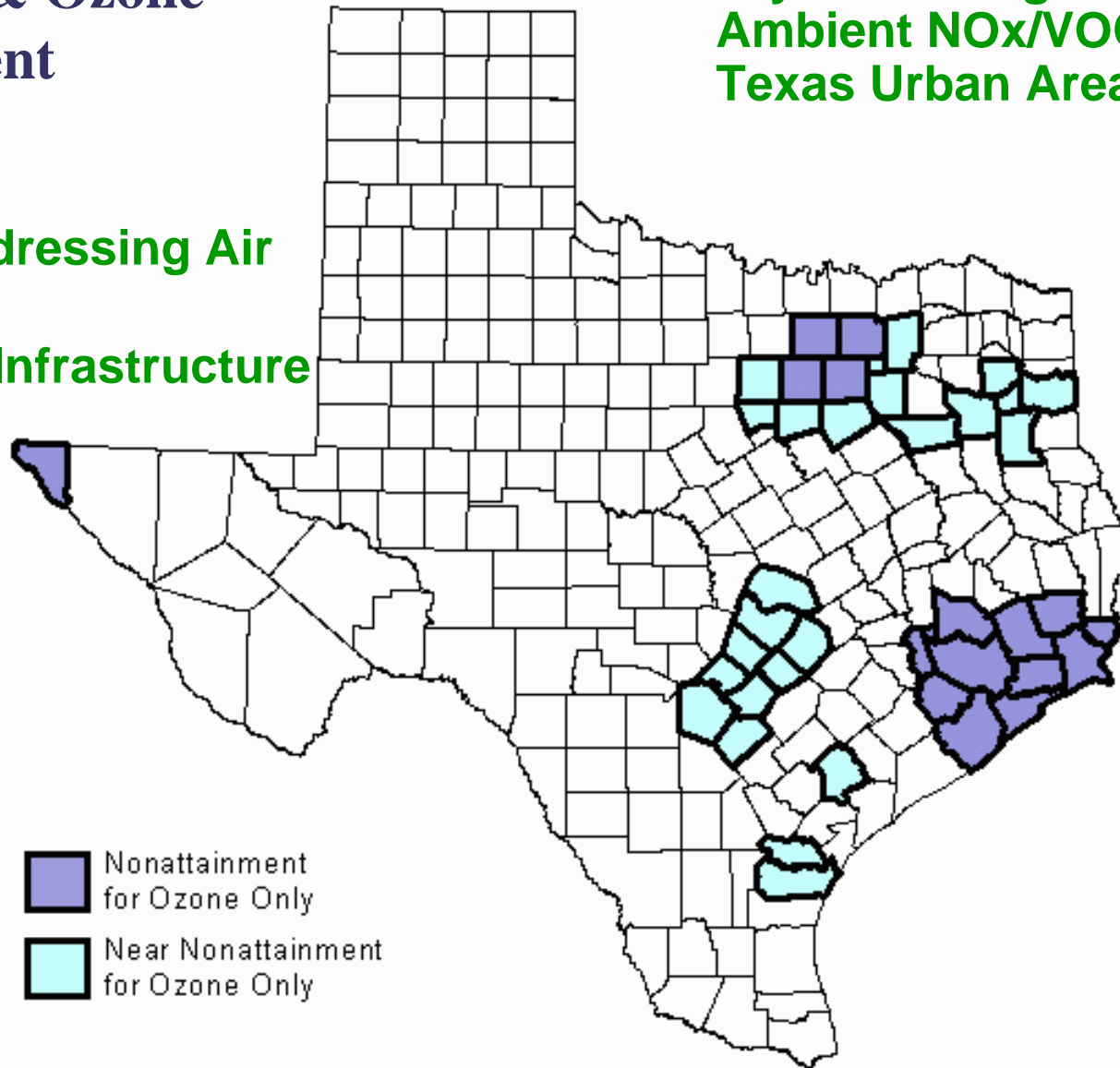
Work of Nature

- **Nearly Maintenance-Free**
 - Only requires Sunlight, Rainfall, and Natural Air Movement.
- **Air turbulence** is constantly carrying the gases over the surface for deposition
- The simulated vertical NO concentration profile on an urban model road showed **the highest concentration occurs on the road surfaces (~800 ppb)**

Air Quality & Ozone Nonattainment

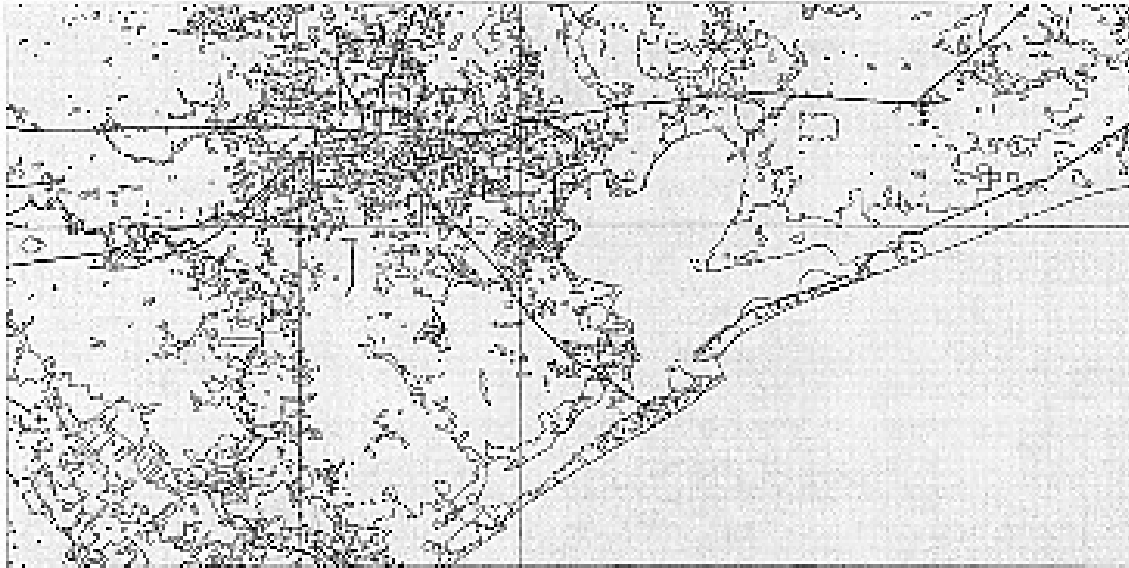
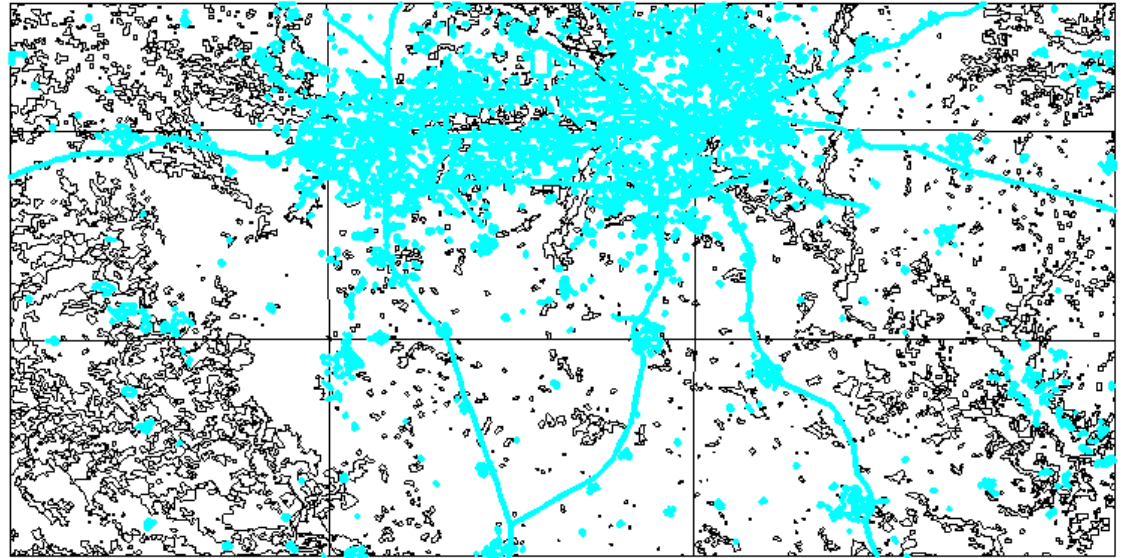
Catalytic Coatings Combat Ambient NOx/VOCs in Texas Urban Areas

Technology Addressing Air Quality through Transportation Infrastructure



http://www.tnrcc.state.tx.us/gis/metadata/nonatain_met.html

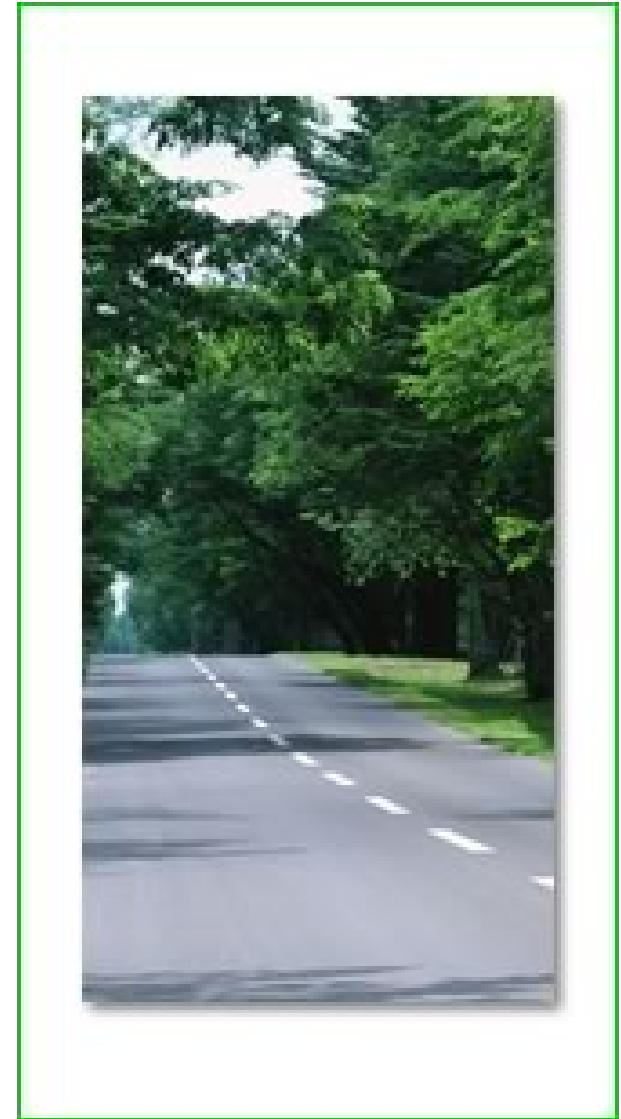
DFW built-up area
= 12200 (km)²



HGB built-up area = 10040 (km)²

City Planning & Green Architecture

- This technology will give architects and town planners a new weapon in the fight against pollution.
- This green construction technology has the potential to reduce the number of high ozone days in the DFW or HGB areas.
- Texas' large urban areas (DFW & HGB) with plenty of sunshine provide an ideal setting for developing and testing the photocatalytic coating technology to facilitate sustainable economical growth in Texas.



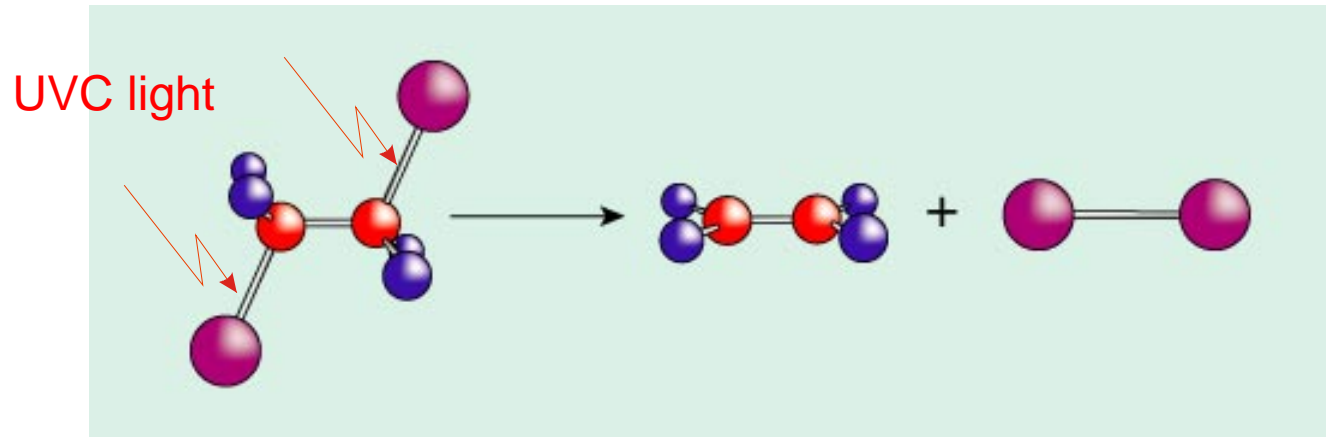
TiO₂ Catalytic Coatings as Noted by TCEQ

- http://www.tceq.state.tx.us/assets/public/implementation/air/sip/miscdocs/area_8-31-05.pdf
- **Area - Potential Control Strategies for DFW Attainment Demonstration**

TiO₂ Catalytic Coating: Cost-Effectiveness

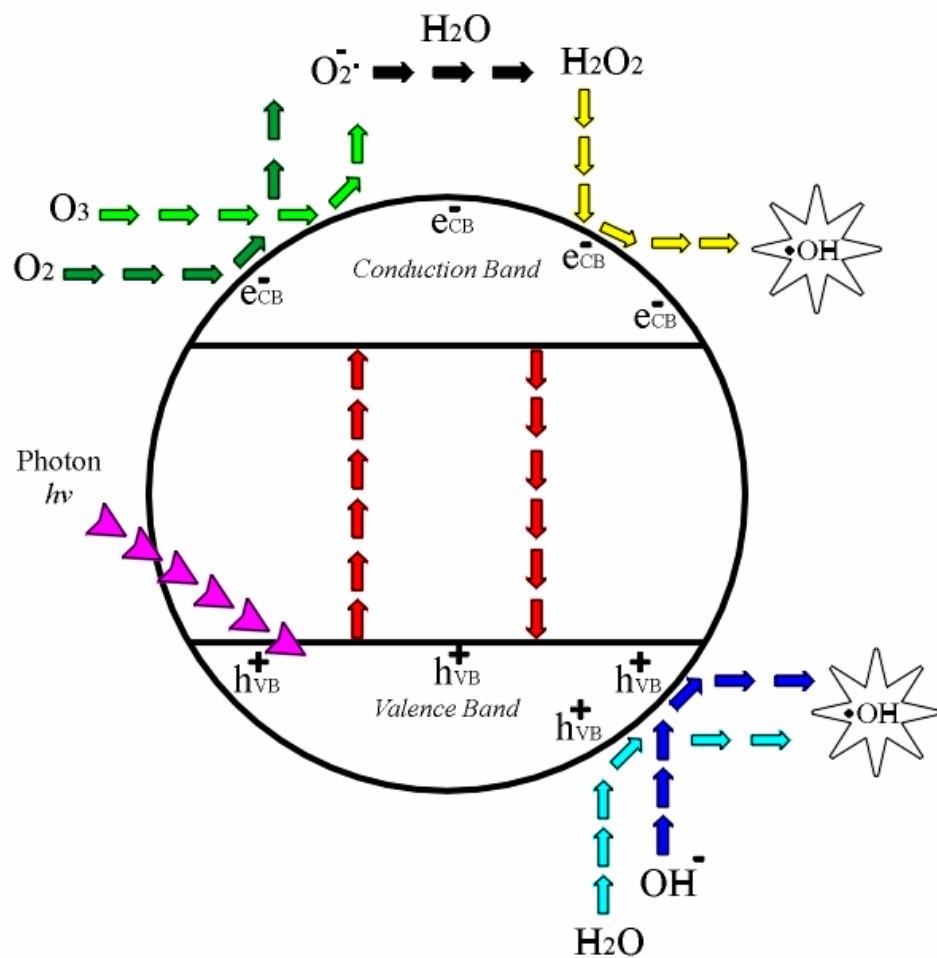
- **Even though the chemistry works for both NO_x and VOCs, the current project will focus on NO_x only.**
- **The preliminary estimate of NO_x removal is very promising (50,000 ton/yr or 28% for Harris County at a cost of \$200/ton assuming pavements last for 5 years).**

Photolysis: High Energy Photons



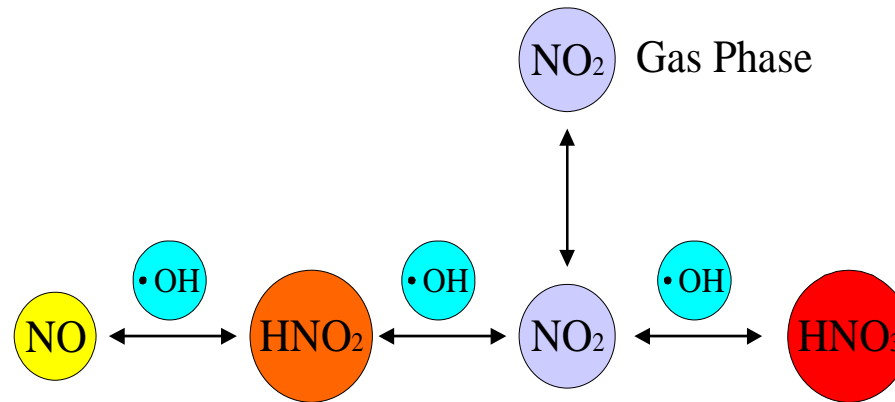
UVC can break the chemical bonds

Photocatalysis: Lower Energy Photons



- **Potential to use sunlight**
- **Ambient T & P**
- **Light-induced electron-hole pairs generating free radicals to start redox reactions**

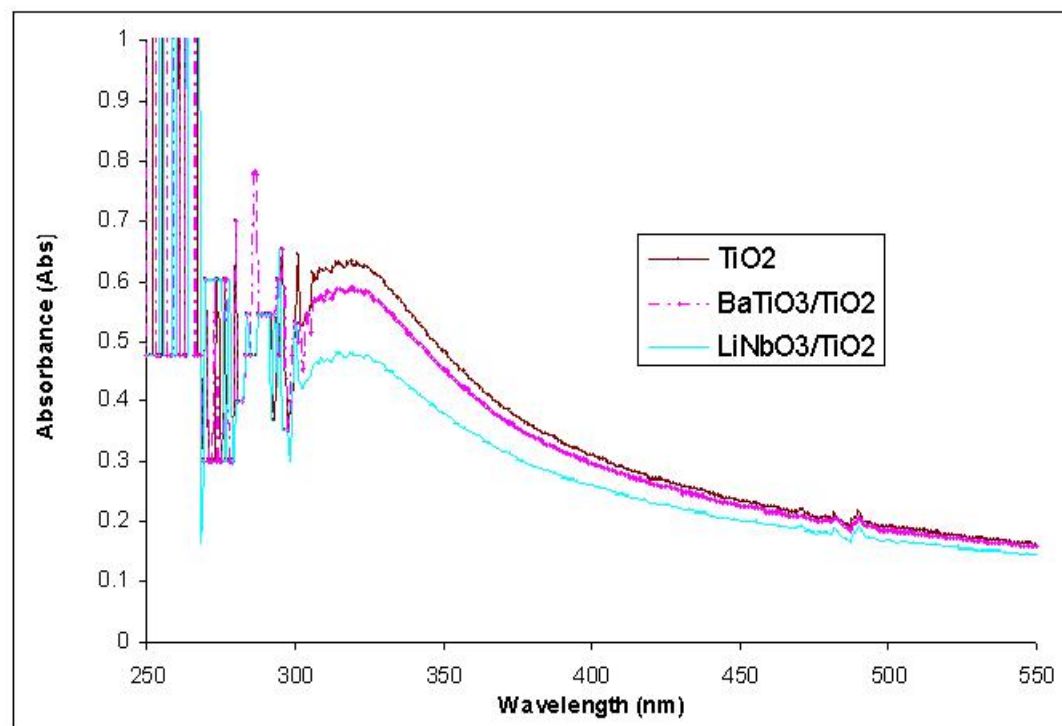
NO_x photocatalytic oxidation



Proposed Tasks

- Technology Update and Preliminary Impact Study
 - Latest developments in removal rate estimate & cost data
 - Estimation of coatable road surfaces (including pavement, sound barrier, road sign, etc.) using GIS
- Lab Investigations
 - Ferroelectric Optical Additive
 - Visible-Light-Responsive Catalyst
 - Advanced Photocatalytic Composite Materials

Lab Investigation (1): Ferroelectric Optical Additives

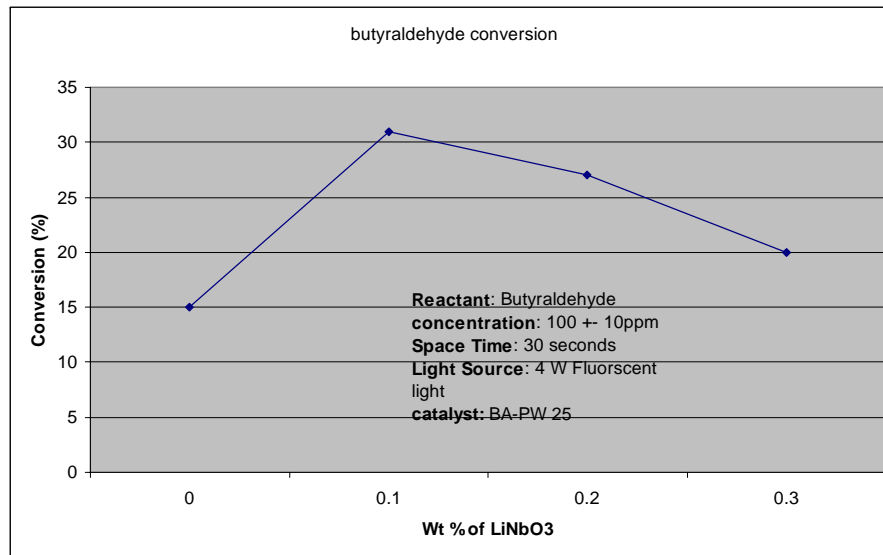


Lamar University has pioneered the use of **wide band gap, high transmittance, ferroelectric crystals** such as LiNbO_3 and BaTiO_3 as additives to utilize UV/visible light more efficiently.

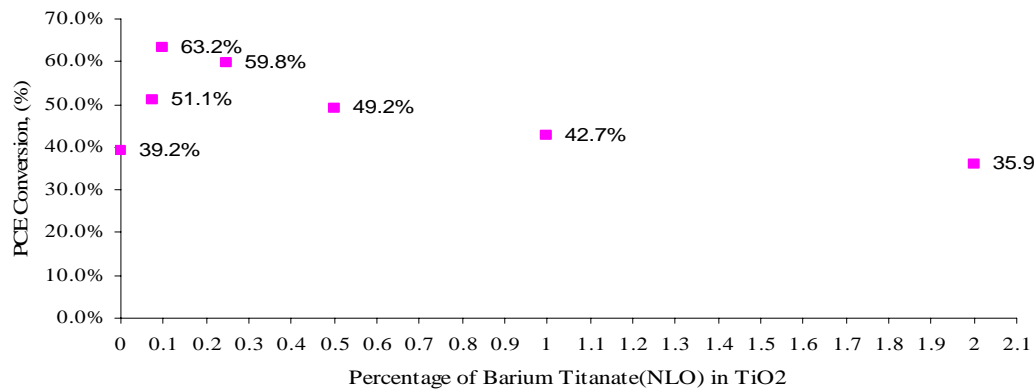
The ferroelectric opticals can **guide UV/Visible light into the catalyst interiors, enhance scattering, and stabilize the electron-hole pairs**

Both BaTiO_3 - and LiNbO_3 - modified TiO_2 's **absorb less in the UVA/Vis. region (300-550nm)** compared to Degussa P-25 TiO_2 .

Enhancements with LiNbO_3 and BaTiO_3 Additives



0.10% (w/w) LiNbO_3 shows a 16% increase in butyraldehyde conversion using visible-light-responsive BA-PW25



0.1% (w/w) BaTiO_3 shows a 24% increase in PCE conversion using P-25 TiO_2

Lab Investigation (2)

- Test **visible-light-responsive catalysts** (e.g., BA-PW 25, TiO_xN_y , TaN) vs. regular UVA light titania (e.g., P-25)
- Lab investigation using **photocatalytic concrete composite materials** for NO_x removal

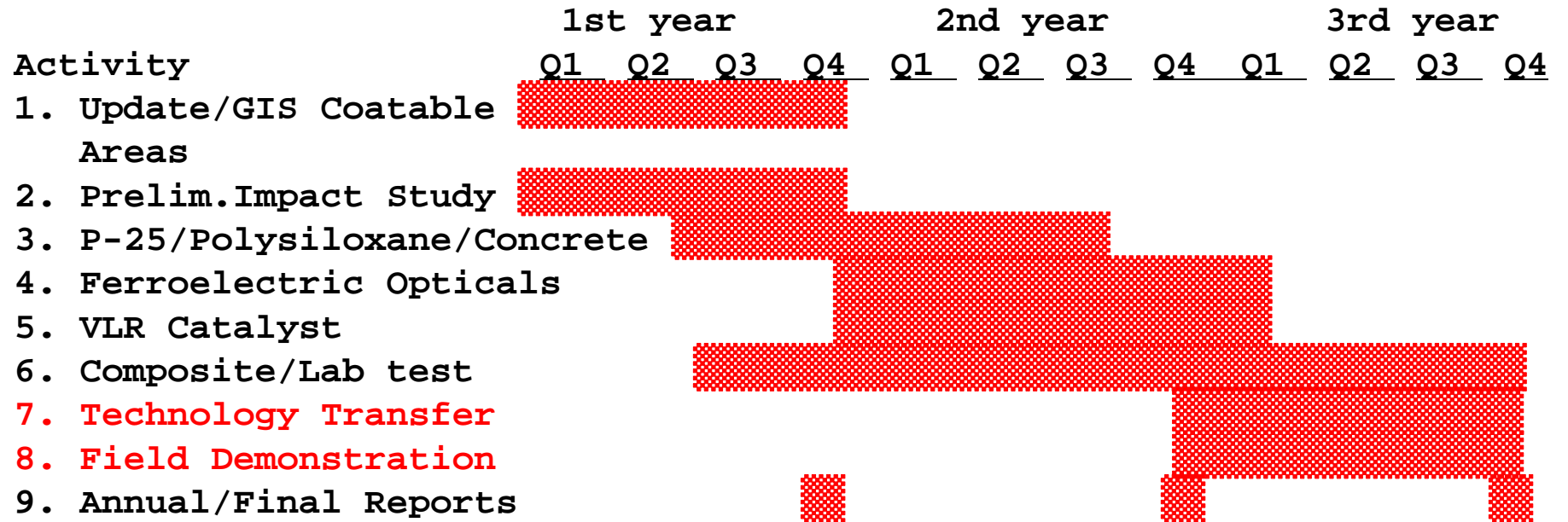
Technology Transfer Partners

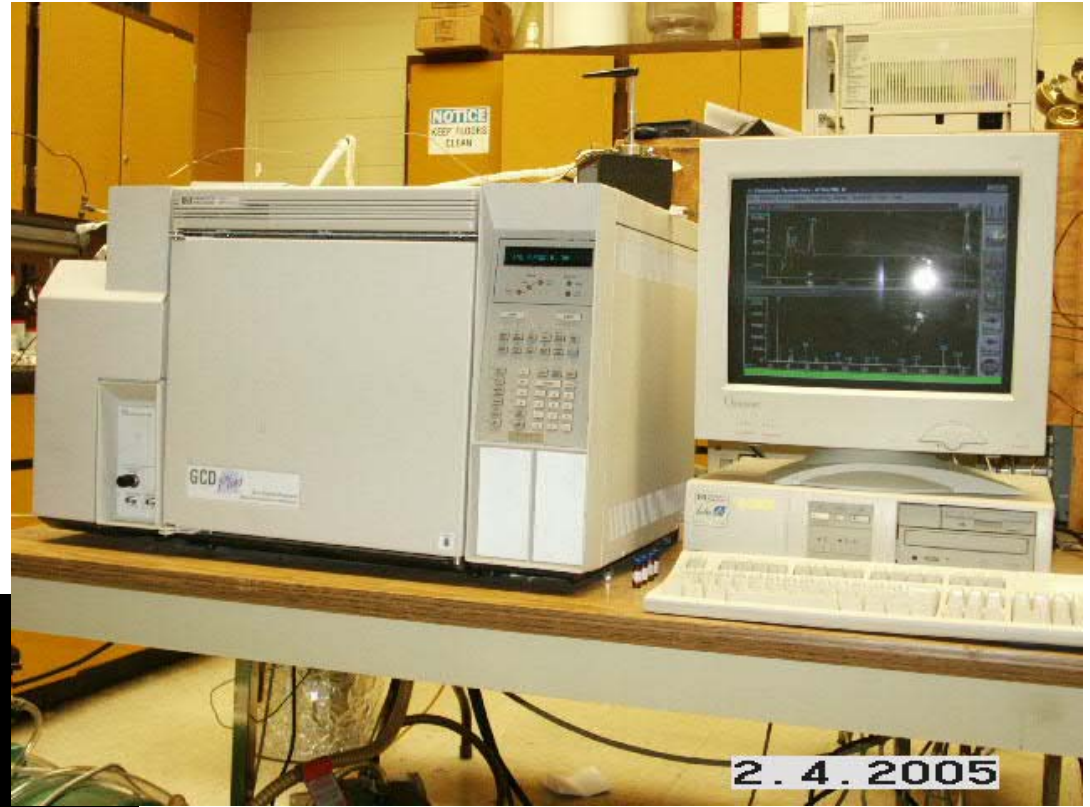
- Concrete & Coating companies
 - Few Ready Mix Concrete Co., Jasper, Texas.
http://concreteproducts.com/mag/concrete_few_ready_mix/
 - Italcementi Group's subsidiary: Essroc

Field Demonstration

- **Demonstrate the developed technology with the approval of community and government agencies (City, TCEQ, TxDOT, EPA).**

Milestone Chart





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Recent Papers/Grants

- X. Ye, D. Chen, K. Li, V. Shah, M. Kesmez, K. Vajifdar, "Photocatalytic Oxidation of Aldehydes/PCE Using Porous Anatase Titania and **Visible-Light-Responsive Brookite**" *Titania Chem. Eng. Comm.*, In Press.
- Ye, X., Chen, D.H., and Li, K. "Oxidation of PCE **with a UV LED Photoreactor**", *Chemical Engineering & Technology*, January 2005.
- "Fiber-Optic Photoreactor Using **Titania Modified with Ferroelectric Optical Crystals** for VOC Destruction," with K. Vajifdar, T. Han, B. Ardoin, D. Grooms, and K. Li, 13th International Congress on Catalysis, Paris, France, July 11-16, 2004
- "**TiO₂ Photocatalytic Oxidation Of Nitric Oxide**: Transient Behavior And Reaction Kinetics" Sid Devahasdin, Chiun-Jr Fan, Kuyen Li, and Daniel H. Chen, *Journal of Photochemistry and Photobiology A: Chemistry*, **156**/1-3 pp 161 – 170 (2003).
- "Photocatalytic Oxidation of Butyraldehyde over Titania in Air: **Byproduct Identification** and Reaction Pathways," with C. Huang, and K. Li, *Chem. Eng. Comm.*, **190**,373-392, 2003.
- "TiO₂ Photocatalytic Oxidation of Butyraldehyde and PCE in the Air through Concentric Reactors," with K. Li, S.Y.C. Liu, C. Huang, S. Esariyaumpai, *J. Adv. Oxid. Technol*, 5(2), 227-232 (2002).
- Grants: **USDA, EPA, Industry**
- **http://hal.lamar.edu/%7Eeche_dept/photocatalysis/homepage.htm**

Dr. Robert L. Yuan, P.E.

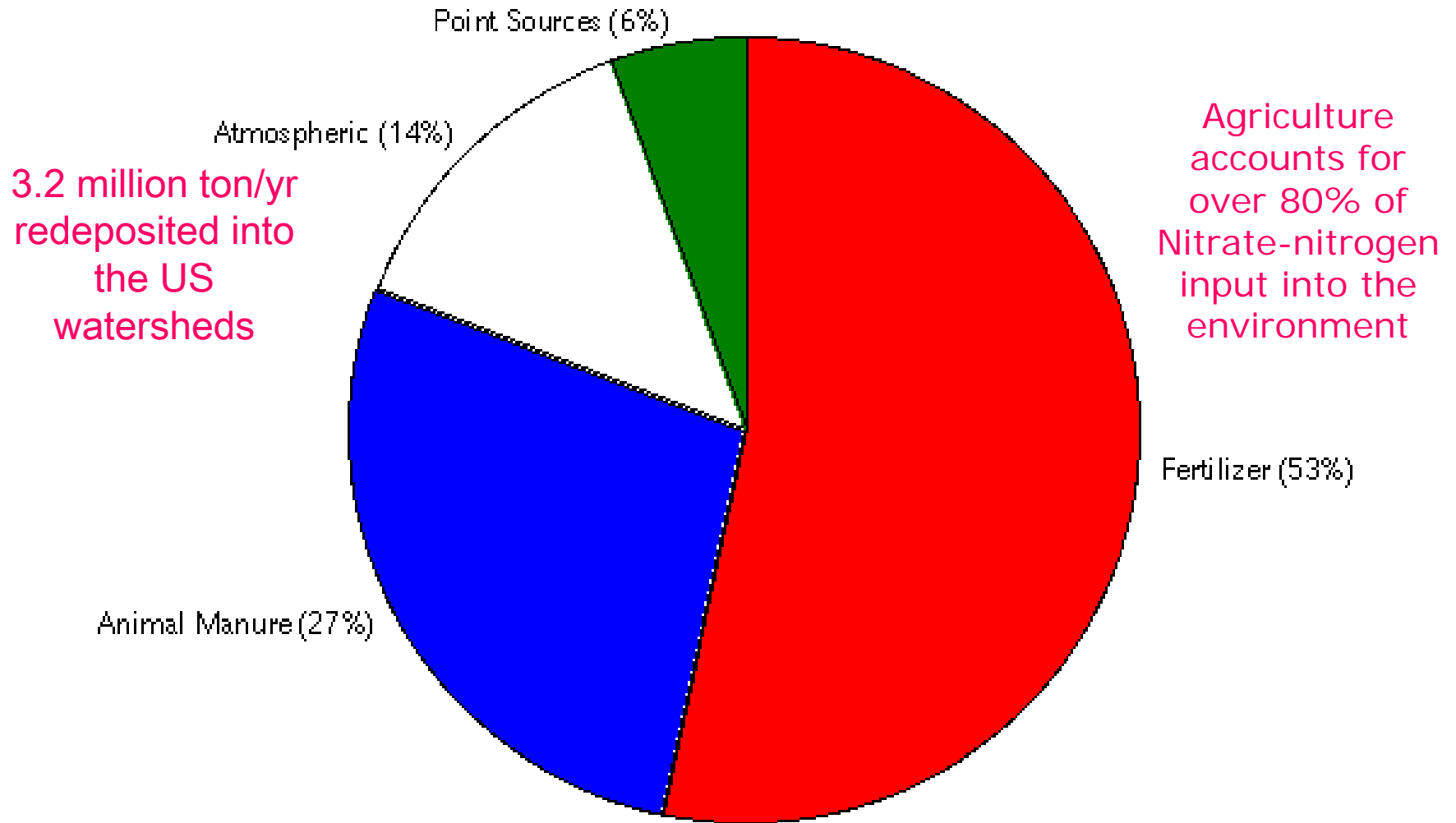
- **Area of Expertise**
 - **Fiber-Reinforced Polymer Composites in Civil Engineering Structural Application**
 - **Properties and Behavior of Plain Concrete Materials, Reinforced Concrete Structures, and Prestressed Concrete Structures**
 - **Experimental Mechanics and Computational Analysis**
- **Full-Scale Testing of Concrete Columns, Composite Columns, Composite Bridges, etc.**



Asphaltic Pavements

- The asphaltic pavements are important to consider
 - **TiO₂ powder** can be easily put on new paved asphaltic surfaces just as active carbon used as a P-25 titania support for enhanced NOx/VOC adsorption.
 - **Lime stone** as part of the aggregate can also be mixed with asphalt to provide neutralization capability.
- In the initial efforts, we would like to focus on cement surfaces. **Asphaltic surfaces will be included in a sister proposal to other agencies.**

Impact of Nitrate



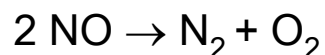
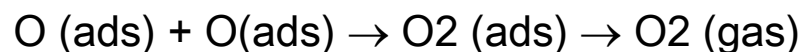
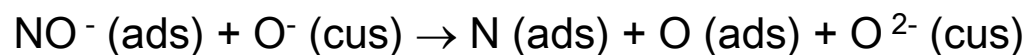
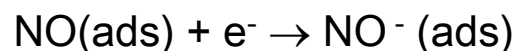
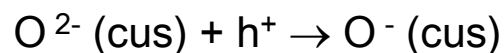
Source: USGS; Nonpoint and point sources of nitrogen in major watersheds in the U.S. (Pucket, 1994) (<http://www.ewg.org/reports/Nitrate/Figure1.html>)

Impact of Nitrate

- Assuming the best (worst?) scenario:
 - For HGA, 2500 km² coated area, the photocatalytic coating is estimated to remove 20,000ton/yr of nitrogen from air.
- That represents a 28% reduction of NO_x in air
 - But only represents 2% of the nitrate-nitrogen to the Gulf of Mexico (total 10⁶ ton/yr nitrate nitrogen in Mississippi River Basin)
- Our preliminary estimate is **the nitrate contribution will not be significant.**
- **Total nitrate increase may be less than estimated because some NO_x emitted into the air will be eventually oxidized and redeposited to water.**

NO Photocatalytic Decomposition

Dissociation of NO:



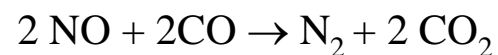
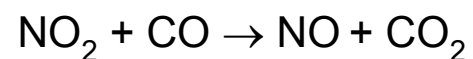
cus: coordinatively unsaturated

ads: adsorbed

N.W. Cant, J.R. Cole, J. Catal. 134 (1992) 317.

NO/NO₂ Photocatalytic Reduction

Reduction of NO/NO₂:

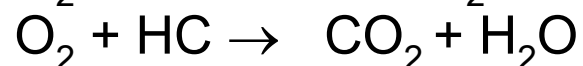
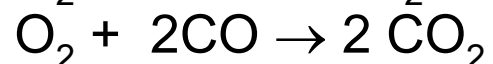
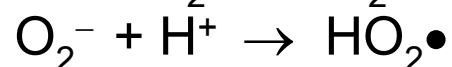
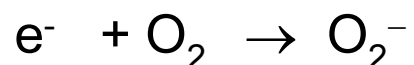
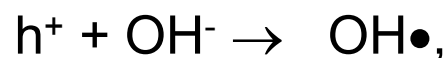


Photocatalytic Oxidation of VOC/CO

Oxidation of VOC/CO:



irradiation

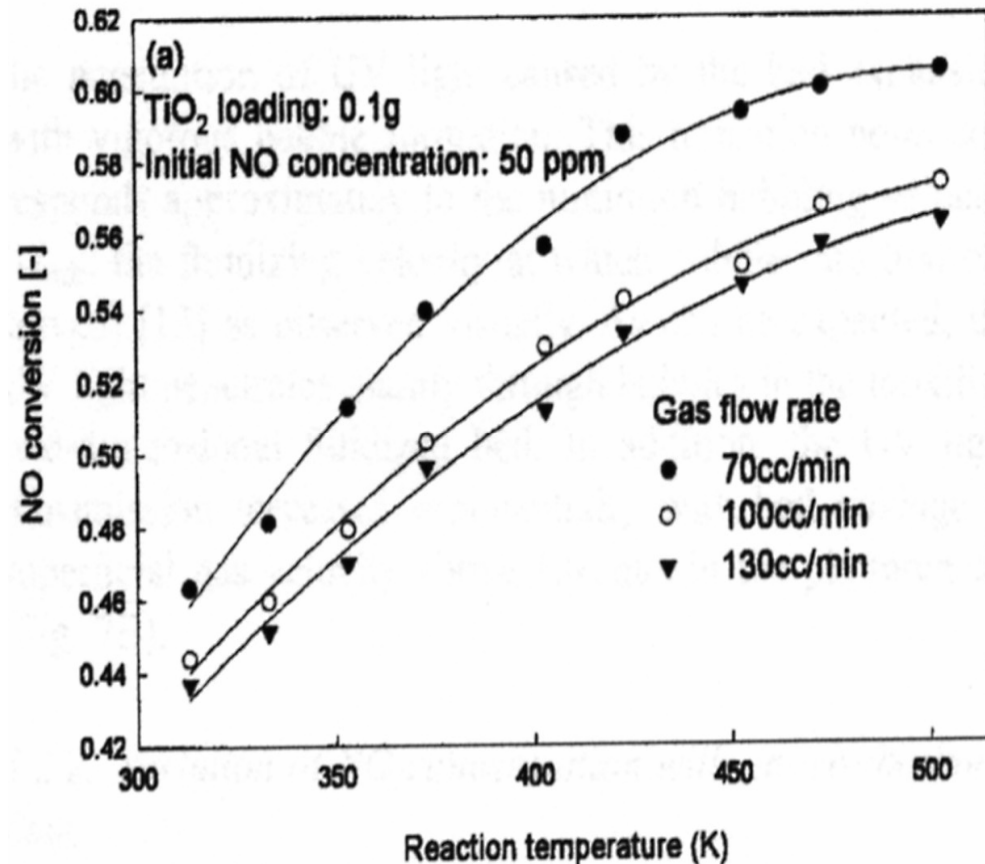


under UV/Vis light

Where HC is a hydrocarbon.

Extreme Weather Conditions

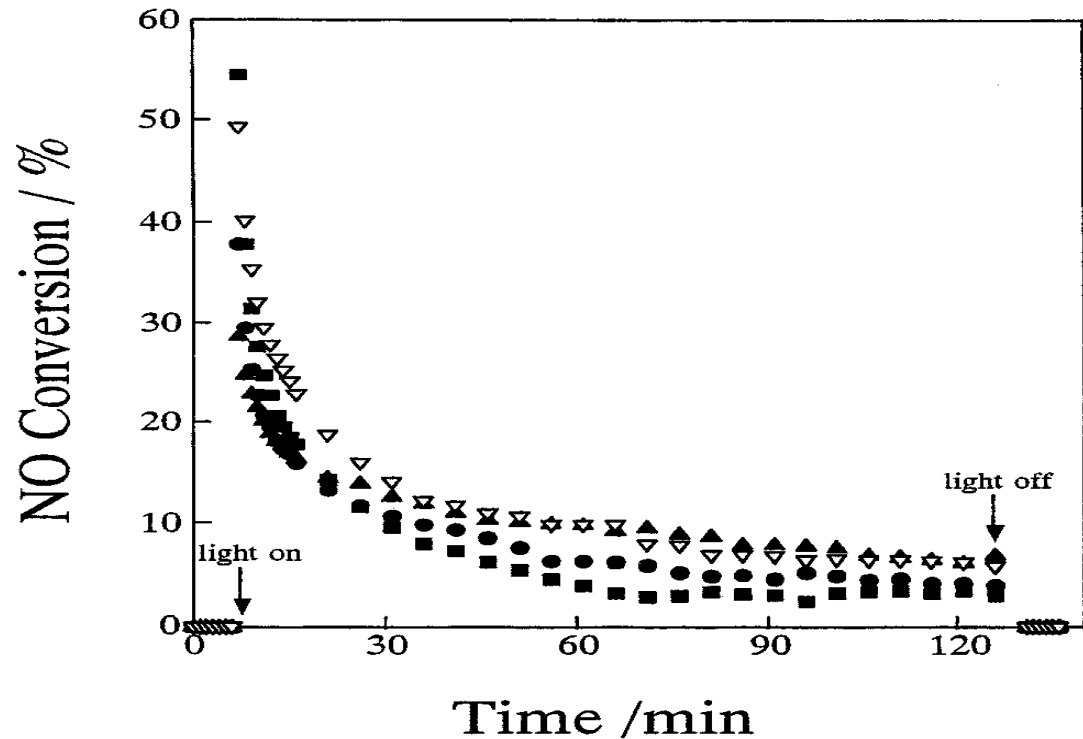
- Temperatures/Humidities are known to go to extremes in Texas
 - Temperature & Humidity impacts will be studied.
- Lim et al. found that NO conversion increases from 48% to 60% from 37°C to 227°C at an initial NO concentration of 50ppm.
- Studies show humidity has a positive effect on NO oxidation up to RH 50% then declines between 50%-80%.



Lim et al. found that NO conversion increases from 48% to 60% from 310K (37C) to 500K (227C) at an initial NO conc. of 50ppm*.

Issue: NO_x Decomposition

- Photocatalysts that decompose NO_x to N₂ and O₂ are available .(N. W. Cant, J.R. Cole, J. Catal. 134 (1992) 317).
- We will include this part in the 3rd year tasks if funded.



Reaction time profiles of the photocatalytic decomposition of NO at room temperature on the TiO₂ photocatalyst pretreated with O₂ at 573 K. Pretreatment: under a flow of O₂ (20 cm³/min) and Ar (20 cm³/min) at 573 K, heated in an Ar flow (20 cm³/min) at 295 K (d), 373 K(j), 473K(m), and 573K(,), respectively. Gas component: 10 ppm NO in He, 100 cm³/min. Catalyst: JRC-TIO-4, 150 mg. *J. of Catalysis*, **198**, 1-8 (2001)

CMAQ Modeling

- CMAQ employed nitrate formation and dry/wet deposition models (e.g., acid, and mercury)
(http://www.cmascenter.org/2003_workshop/session3/morris_abstract.pdf)
- We agree that
 - it is beneficial to use the CMAQ model in sensitivity mode to demonstrate the effectiveness/impact of this approach.
 - it is beneficial to incorporate the NO_x deposition model on heterogeneous surfaces into the future CMAQ package).
- However, experiments need to be conducted first in order to generate good data of NO_x deposition flux