

# Can we increase concrete durability with nanoparticles?

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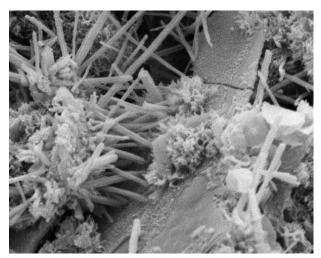


Georgia Institute for Electronics and Nanotechnology



# Concrete is incredibly complex

- Pre-hydration it has at least 5 components
- Post hydration, has at least 5 new components



http://www.cementlab.com/cement-art.htm

Before Hydration	
Compound	% by weight
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	10
$Ca_4Al_2Fe_2O_{10}$	8
$Ca_2SiO_5$	20
Ca <sub>3</sub> SiO <sub>4</sub>	55
Na <sub>2</sub> O	Up to 2
K <sub>2</sub> O	
CaSO <sub>4</sub> .2H <sub>2</sub> O	5

http://www.engr.psu.edu/ce/courses/ce5 84/concrete/library/construction/curing/ Composition%20of%20cement.htm

# Corrosion is a major source of durability loss in concrete



https://theconstructor.org/concrete/durability-of-reinforced-concrete-to-environment/8894/



Image from Dr David Scott

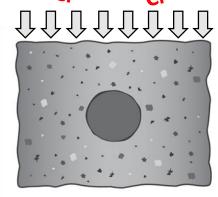
# But it's more costly than just loss of durability

- $\sim$  5% of an industrialized nation's income is spent on it
- In the U.S., 3.2% of the GDP
- Average bridge in the U.S. is 43 years old
- 9.1% of U.S. bridges structurally deficient



Image from Dr. David Scott

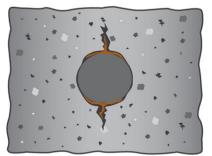
# Chloride ions destroy the passive layer that protects concrete from corrosion

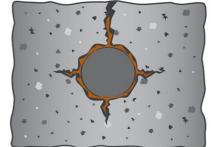


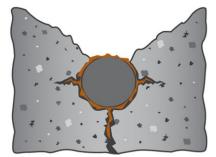
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CI.

**C**/.







**BEFORE CORROSION.** 

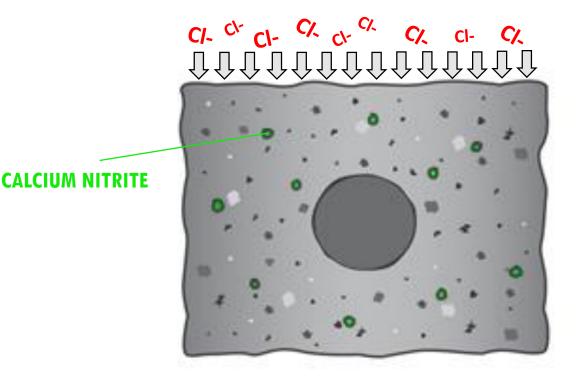
#### BUILD-UP OF CORROSION PRODUCTS.

#### FURTHER CORROSION. SURFACE CRACKS. STAINS.

#### EVENTUAL SPALLING. CORRODED BAR. EXPOSED.

https://theconstructor.org/concrete/corrosion-steel-reinforcement-concrete/6179/

# Previous solutions have involved calcium nitrite or nitrate



CALCIUM NITRATE BECOMES CALCIUM CHLORIDE AND NITRITE

 $Fe^{2+} + 2 OH^{-} + 2NO_2^{-}$  $\rightarrow Fe_2O_3 + 2NO + H_2O$ 

HELPS REGENERATE PASSIVE LAYER

# Why can't we use what we already have: $NO_x$



http://www.icopal-noxite.co.uk/nox-problem/nox-pollution.aspx

# $NO_x$ is one the components needed to create smog



http://www.huffingtonpost.com/2013/12/09/china-smog-benefits-advantages-state-media\_n\_4413043.html

# Our plan: use $TiO_2$ 's photocatalytic properties in cement to bring in $NO_x$ from the air



http://www.european-coatings.com/Homepage-news/Permanent-changes-to-titanium-dioxide-industry

# **Sample Preparation**

# First, cement plates had to be crushed

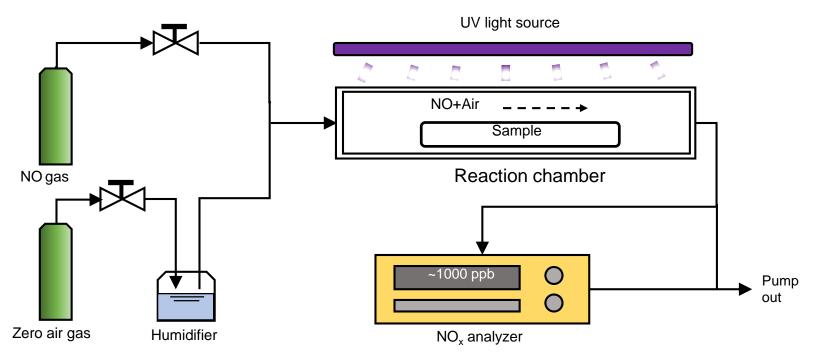


- Plates are 5% TiO<sub>2</sub> by mass
- Final particle size was between 0.6 and 1 mm

### The crushed particles were then exposed to NO gas and UV light

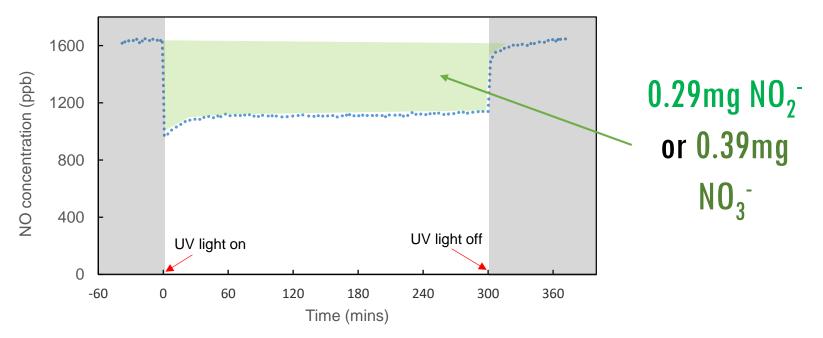


### Samples were exposed to the UV light for 5 hours



# We can estimate $NO_x$ taken in by the concrete

**OPC+5%TiO<sub>2</sub>** (Powder)



# Testing

# X-Ray Diffraction (XRD) works best for crystalline samples

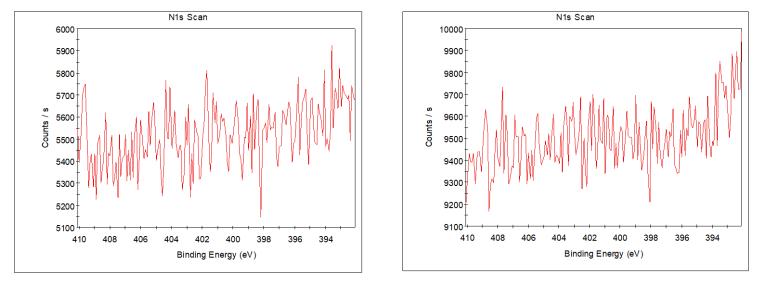
#### • Could not detect nitrogen species



http://mcf.gatech.edu/capabilities/x-ray-diffraction/

#### Nitrogen was not detectable through x-ray photoelectron spectroscopy (XPS), either

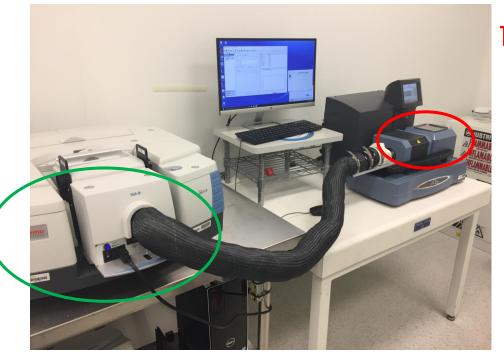
#### **Before UV**



#### After UV

#### We used TGA/FT-IR to look at gas release under decomposition

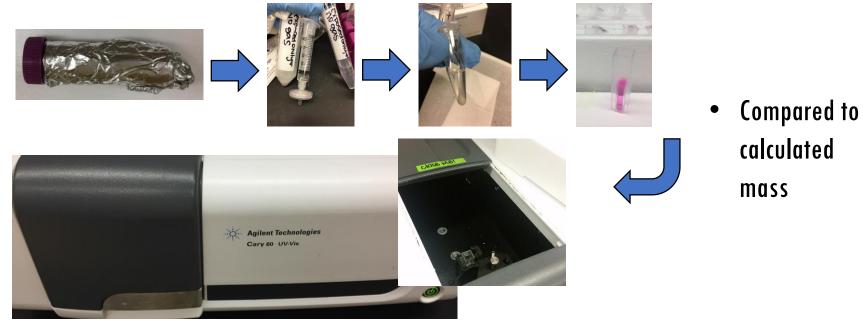
FTIR: to detect released gas



# TGA: to heat the sample

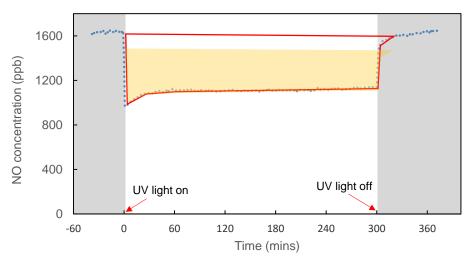
 There was no detectable nitrogen gas or any sort of nitrogen compound

# We used UV-Vis and wet chemical extraction to look at nitrite concentration



Images by Bill Jin

# Good news: found nitrites



#### OPC+5%TiO<sub>2</sub> (Powder)

# Bad news: corresponded to at most 70% of NO<sub>x</sub>

# Where does the nitrogen go?



http://knowyourmeme.com/photos/1231999-stock-photography

### We looked at nitrate mixed with HCI with UV-Vis

- Before: we'd tried to just use a color reagent and could not find nitrate
- Now: we found some

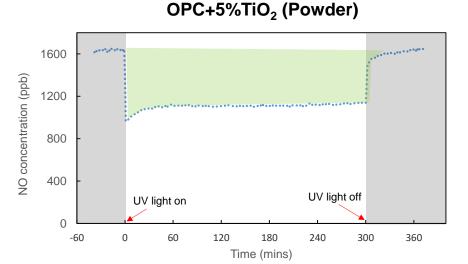


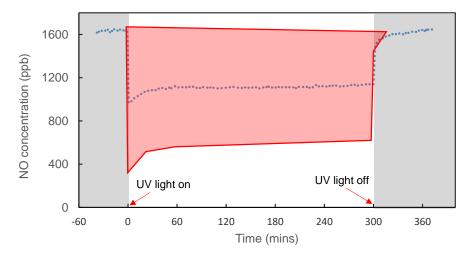
http://mmrc.caltech.edu/Cary%20UV-Vis%20Int.Sphere/Cary%20UV-vis.html

# ... We found too much nitrate

Known: 70% NO<sub>2</sub><sup>-</sup> Assume: 30% NO<sub>3</sub><sup>-</sup> Known: 70% NO<sub>2</sub><sup>-</sup> Known: 200% NO<sub>3</sub><sup>-</sup>

OPC+5%TiO<sub>2</sub> (Powder)



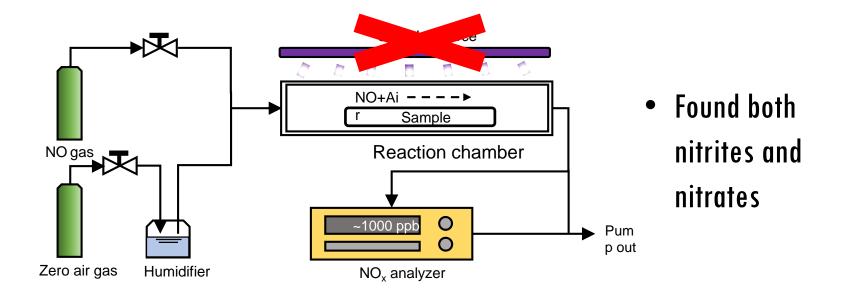


# Where did the nitrogen come from?



# Theory: $NO_x$ is being taken in even when not exposed to UV

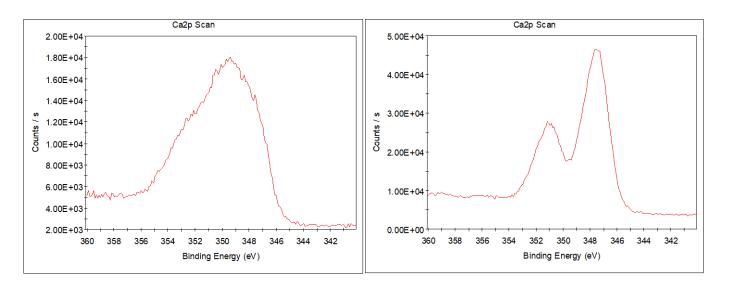
# Now we decide to add a different exposure: NO gas only



# The non-NO<sub>x</sub> information may lead us in a new direction

#### **Before UV**

#### After UV



- XPS shows a marked difference in calcium
- That along with XRD indicates calcium hdroxide

# In Summary...

- Nitrites and nitrates were present in the exposed cement
- NOx abatement also occurs without UV light
- The nitrogen is either amorphous, or does not significantly shift the crystalline structure
- Calcium hydroxide might be the significant phase in the reaction

# More tests are needed in the future

- More NO<sub>x</sub> only runs
- Pure phase runs
- Corrosion tests





Right Image by Dr. David Scott

# Special thanks to...

- Bill Jin
- Dr. Kimberly Kurtis
- Dr. Yuanzhi Tang
- Leslie O'Neil
- Nancy Healy
- Georgia Tech Institute for Electronics and Nanotechnology
- Cleanroom and Mechanical Characterization Facility staff
- The Kurtis Lab







# References

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# **Any Questions?**