Effects of Titanium Dioxide Nanoparticles on Structure and Performance of Cementitious Materials

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Georgia Institute of Technology

A bit about me, my research group, and CEE at Georgia Tech…

- PhD in Civil Engineering (1998) from UC Berkeley
- For 14 years, I've been a professor in the School Civil & Environmental Engineering at Georgia Tech in Atlanta where my research and teaching center on construction materials
- CEE at Tech enrolls ~800 undergrads, ~400 graduate students, with ~60 faculty
- Currently, my research group consists of 1 Post-Doc, 8 PhD students, 1 MS student, and 6 undergraduate researchers

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CEE at Georgia Tech: By the Numbers

745
UNDERGRADUATE
students

357
GRADUATE
students

56
tenure-track
FACULTY

undergraduate programs

No. 3 CIVIL ENGINEERING

No. 2 ENVIRONMENTAL ENGINEERING

graduate programs

No. 4 CIVIL ENGINEERING

No. 5 ENVIRONMENTAL ENGINEERING

$18
MILLION
in new research
funding FY 2012

3 CORE VALUES:

- Rigor
- Diversity
- Entrepreneurial spirit

Overview of Trends in Cement-Based Materials Research

Historically, innovations in construction materials technology have spawned new applications which have changed the ways in which we construct, while increasing efficiencies.

Image: Concretecontractor.com

"Age of Strength"
- WRA chemistry
- SCMs
- Lower w/cm

→ High Strength Concrete (HSC)

"Age of Sustainability"
- Type LS cement
- 3rd series cements
- ???

→ ??C

What innovations will this new age bring?

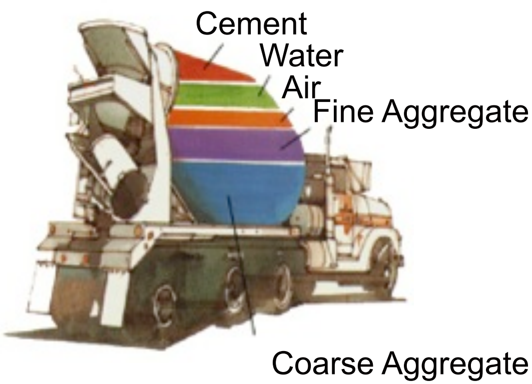
1970 — 1980 — 1990 — 2000 — 2010

"Age of Performance"
- Renewed emphasis on durability
- New admixtures (SRAs, VMAs)
- New additives (SAPs, nanoparticles)

→ High Performance Concrete (HPC)

Sustainable Concrete

- Much of the effort to address concrete sustainability has centered on reducing the environmental impacts associated with the cement



Embodied Energy for Cement and Concrete Production

	% by weight	Btus per ton: Materials	Btus per ton: Hauling	Btus/yard concrete	Energy %
Cement	12%	5,792,000	504,000	1,574,000	94%
Sand	34%	5,000	37,000	29,000	1.7%
Crushed Stone	48%	46,670	53,000	100,000	5.9%
Water	6%	0	0	0	0%
Concrete	100%	817,600		1,700,000	100%

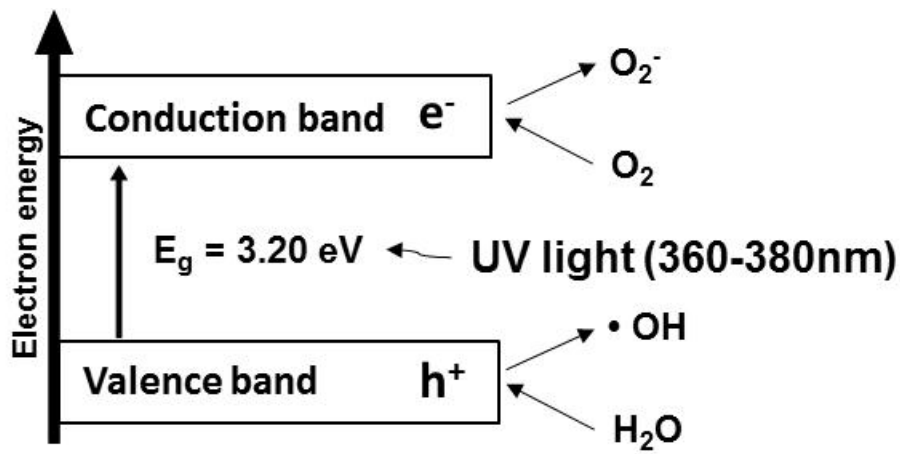
Traditional cement manufacture:

- Utilizes virgin materials: 1.5t raw material → 1t cement
- Liberates CO_2: $CaCO_3$ –heat-> $CaO + CO_2$ (↑)
- Energy intensive: 6-8% worldwide fuel consumption
- Fossil fuel intensive

LCA Source: PCA, SN3001

Sustainability: TiO_2 Nanoparticles

- Spurred by increasing value of sustainability, growing interest in **titanium dioxide (TiO_2)** use in construction materials to create photocatalytic coatings and materials.
- Photocatalysis most efficient: nanoparticles, anatase crystal structure
- In the presence of near-UV/UV radiation ($h\upsilon$), oxygen, and water, a chain of photochemical surface reactions occur → Strong oxidizing capability
- Can oxidize **NOx** ($NO+NO_2$), organic (VOCs), inorganic compounds



Reduction

$$e^- + O_2 \rightarrow O_2^-$$
$$O_2^- + H^+ \rightarrow HO_2$$
$$HO_2 + \mathbf{NO_2} \rightarrow HNO_2 + O_2$$

Oxidation

$$h^+ + H_2O \rightarrow \bullet OH + H^+$$
$$\mathbf{NO_2} + \bullet OH \rightarrow HNO_3$$

- Chemically inert , biologically inert, non-toxic, low cost

  → Good for use in the field

Introduction

- Unique functionality of TiO_2-containing construction materials

NOx binding (Smog abatement):
Minnesota new I-35W
bridge sculpture

Self-cleaning:
Jubilee church

Self-cleaning:
TiO_2 coated/uncoated wall

Day 0 Day 7

Biocidal application:
Alternaria & aspergillus (fungus)

Giannantonio, Kurth, Sobecky, Kurtis, *Int. Biodet. Biodegrad.*, 2009.

Research Questions

Way back in 2008, we asked some questions:

- How do TiO_2 nanoparticles affect portland cement hydration, if at all?
- Are the structure and properties of the cementitious host affected by the presence of TiO_2 nanoparticles?
- How effective is nanostructured TiO_2 in NOx binding on concrete surfaces?
- How does TiO_2 –nanoparticle concrete fit within the context of sustainable development?

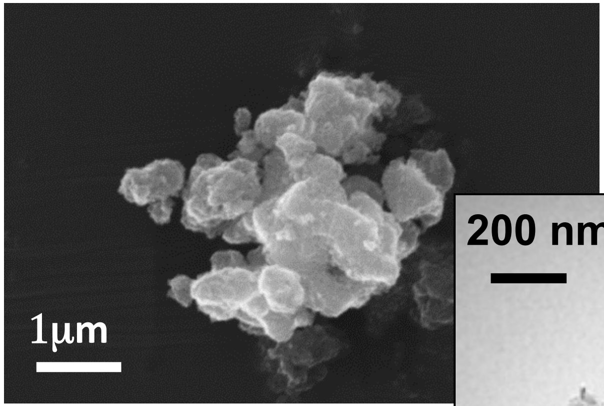
Materials and Sample Preparation

TiO_2 powders obtained from commercial sources

Size: (T1>T2>T3)

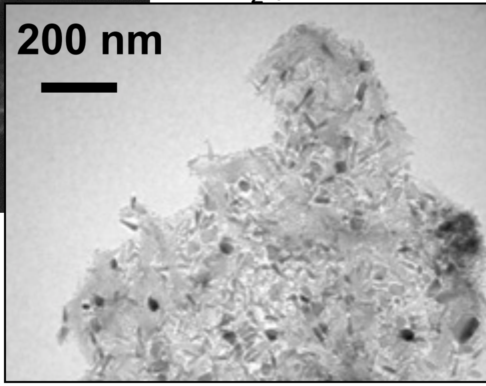
	Particle Size (nm)	Agglomerate Size (μm)	Surface Area (m^2/g)	Purity (%)
T1	20-30	1.5	45-55	>97
T2	15-25	1.2	75-95	>95
T3*	21	0.58	50±15	99.5

* good dispersion



SEM image of TiO_2 powder(T1)

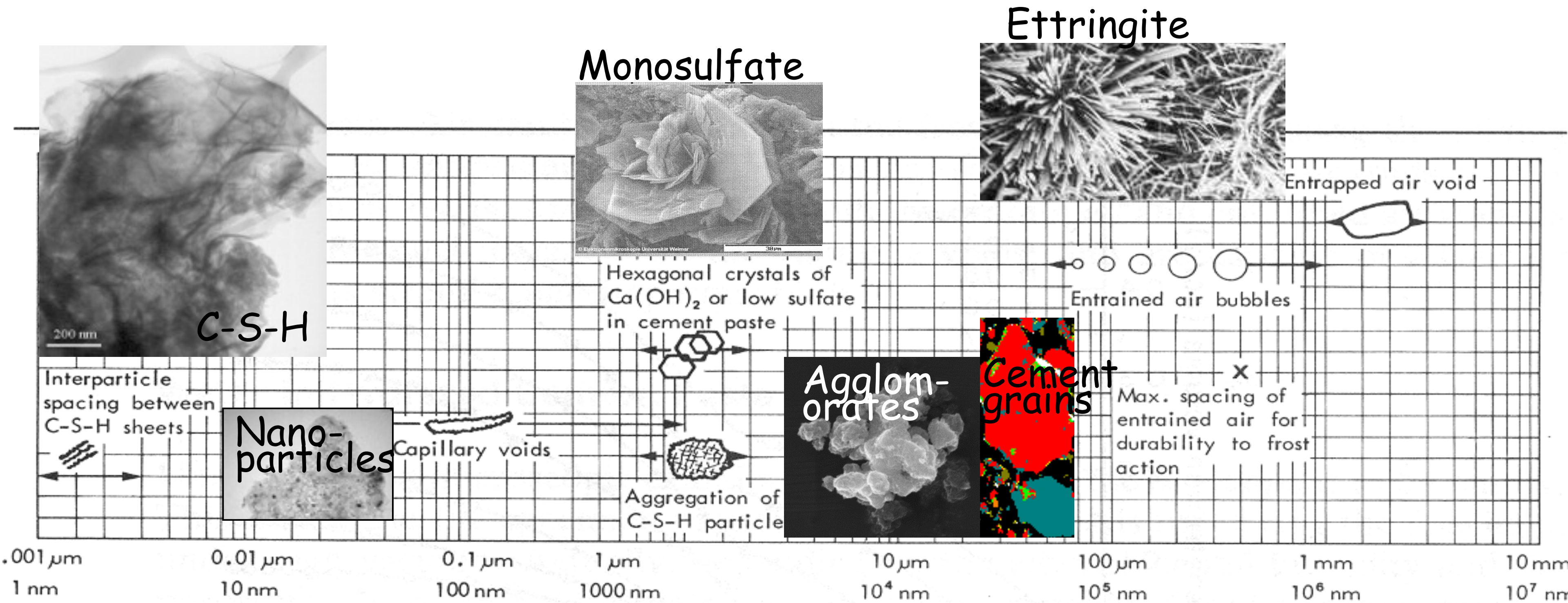
TEM image of TiO_2 powder



- Type I portland cement: median diameter=10.08 μm
- Water-to-solids ratio (w/s) = 0.50
- Filler: 5%, 10%, and 15% weight replacement for cement
- Nanoparticles added to water, ultrasonicated

Materials and Sample Preparation

Multi-scale structure of cement-based materials



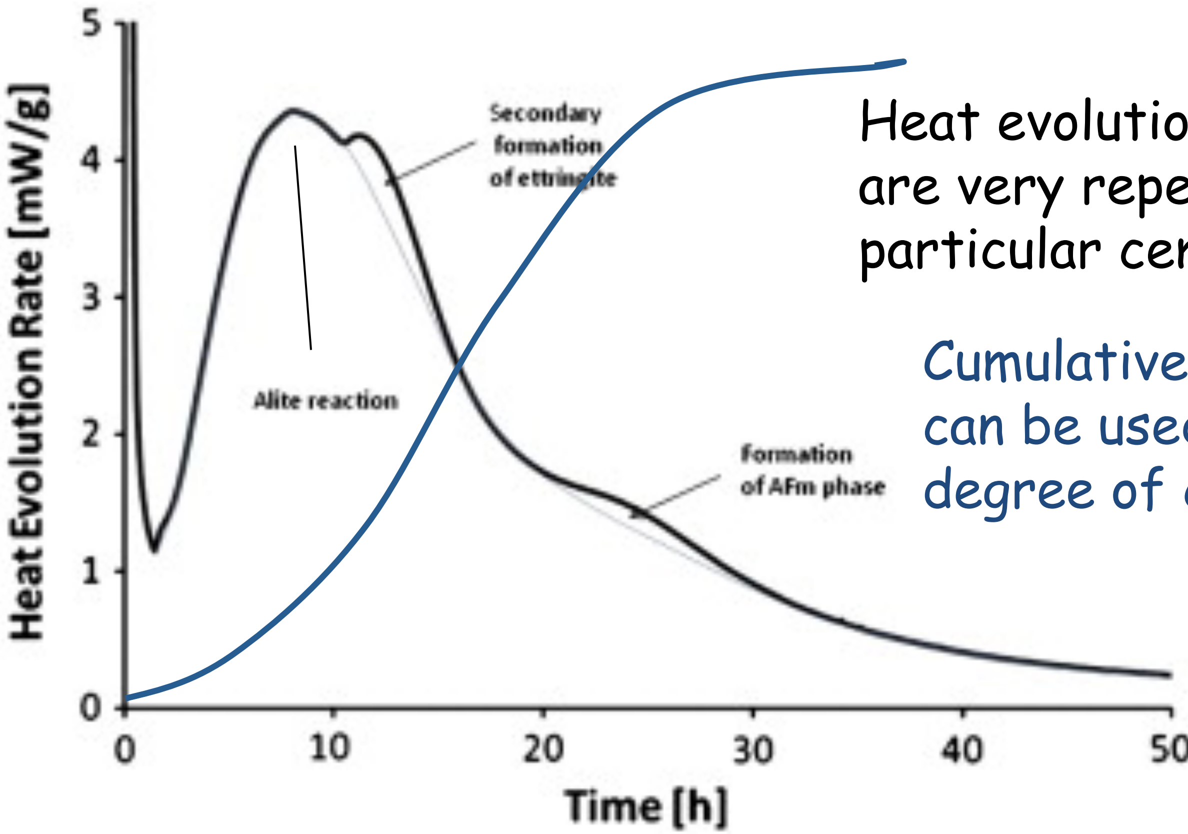
C-S-H image credit: Dr. Eric Lachowski, S.Y. Hong, and F.P. Glasser via Concrete Microscopy Library at UIUC

Cement image credit: NIST, VCCTL

Table and monosulfate and ettringite image credits: M&M text

Cement Hydration

- Isothermal calorimetry is a technique used to examine reaction rates (or kinetics), measured through heat evolved during cement hydration



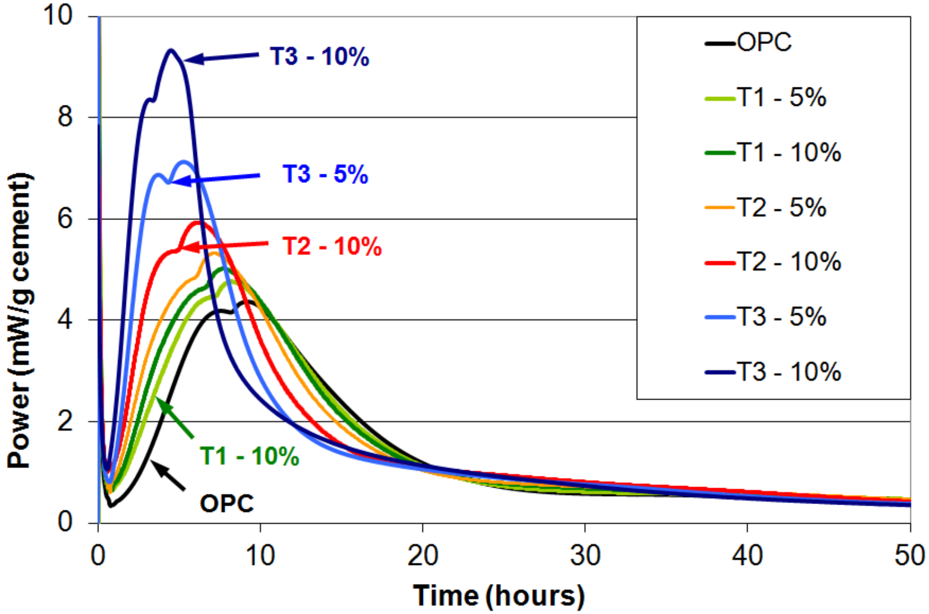
Heat evolution with time curves are very repeatable for a particular cement.

Cumulative heat of hydration can be used to determine degree of cement reaction, α.

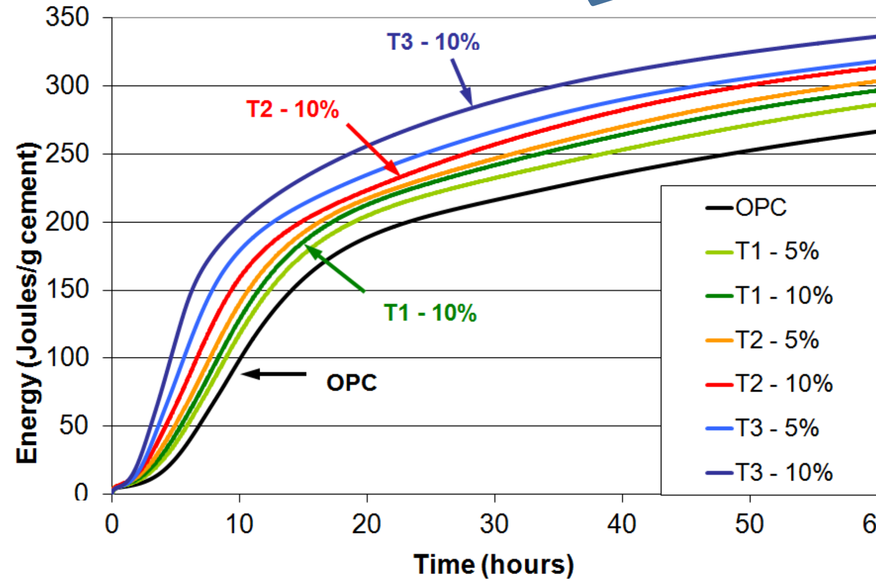
Bullard et al, *CCR,* 2011.

Effect on Hydration

cement



Rate of hydration of TiO_2-blended cements



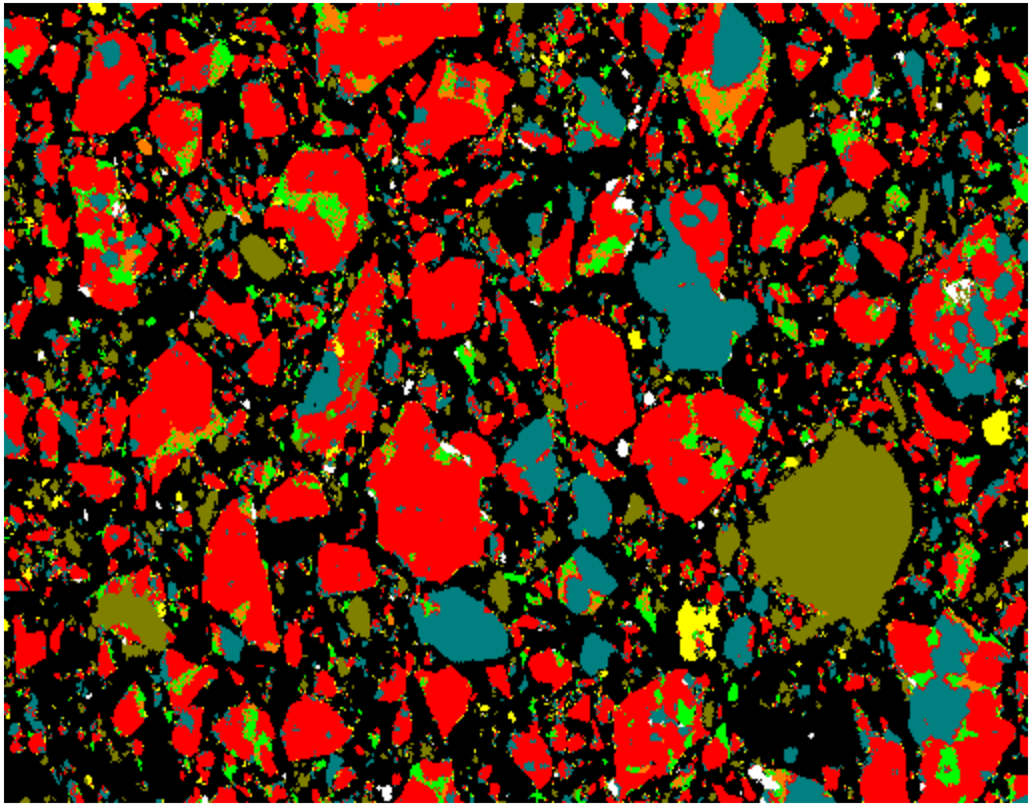
Total heat evolution of TiO_2-blended cements

- TiO_2 nanoparticles accelerated the rate of hydration, increased peaks
  - T3 (280min) > T2 (180min) > T1 (80min)
- Increasing TiO_2 dosage, dispersability -> greater degree of hydration (α)
  - Total heat evolved T3 (34%)>T2 (27%)>T1 (18%) increase compared to OPC

Chemically inert nanoparticles accelerate cement reactions and promote greater degree of early hydration.

Jayapalan, Fredrich,Lee, Kurtis *Transportation Research Record*, 2010.

Effect on Hydration



Recall that portland cement is composed of mineral phases, including:

Tricalcium silicate (C_3S)

Dicalcium silicate (C_2S)

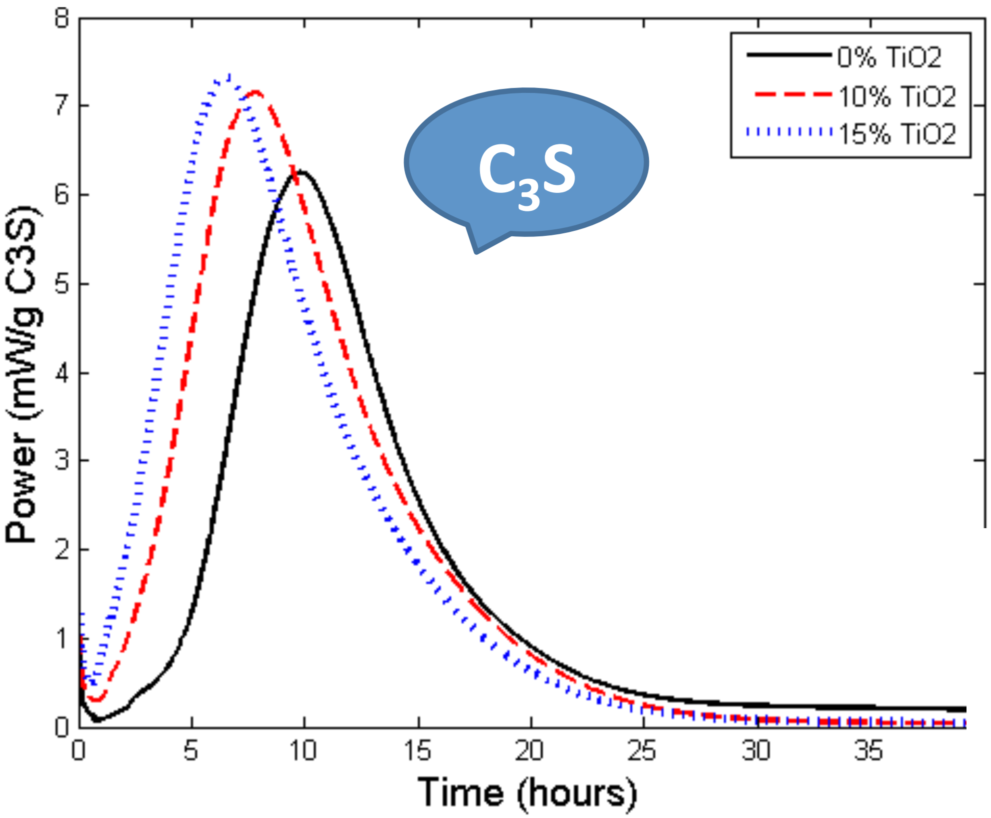
Tricalicum aluminate(C_3A)

Tetracalcium aluminoferrite (C_4AF)

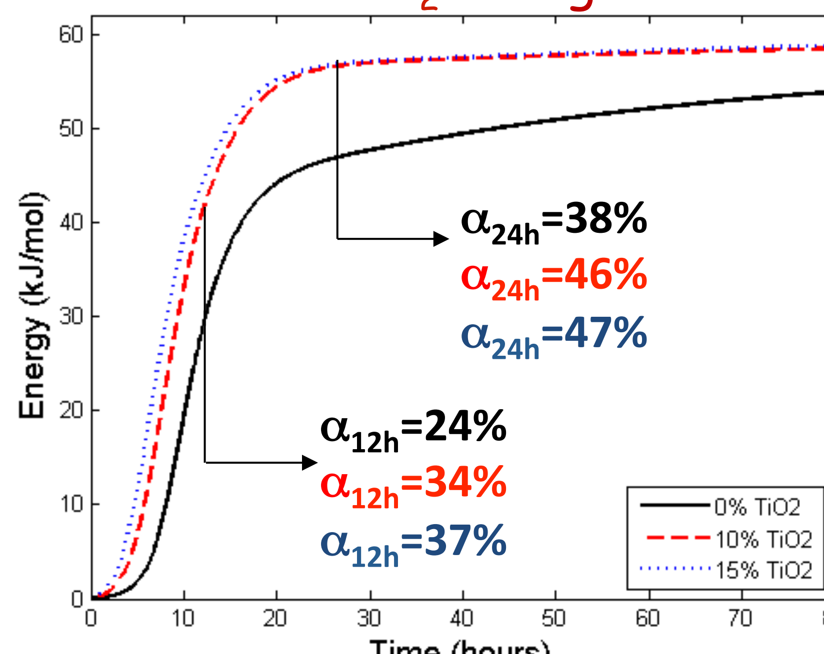
Gypsum ($C\bar{S} \cdot 2H$)

Effect on Hydration: C_3S

What are the effects of nanoparticles additions to cements?



- Acceleration: ~120 min (10%) and ~200 min (15%)
- Increase in peak rate height, which increases with TiO_2 addition rate
- Total energy evolved and degree of hydration (α) are directly related to TiO_2 dosage

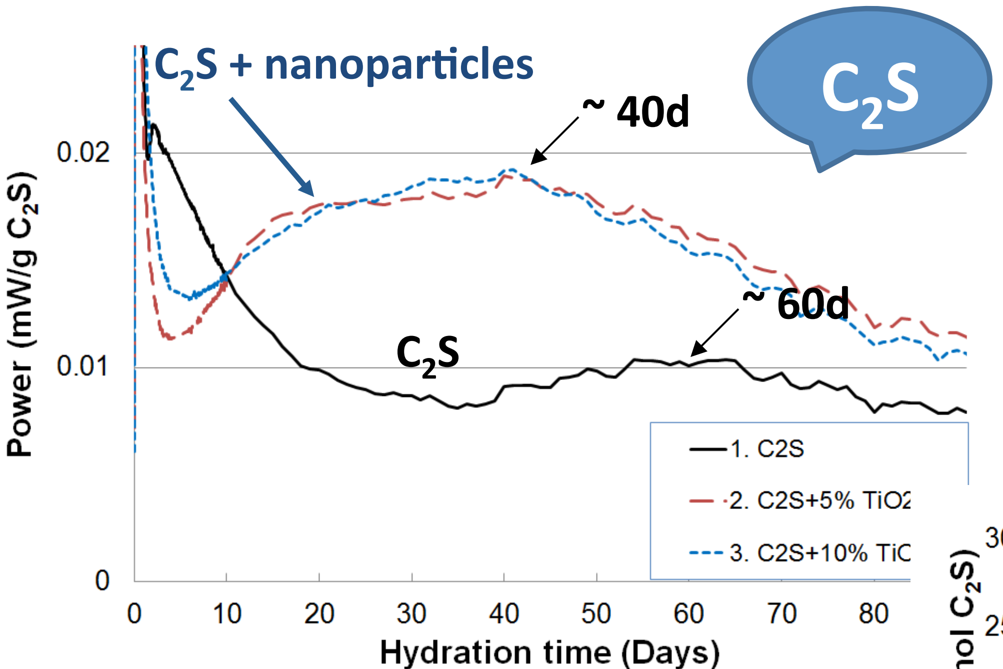


Initial evidence that inert TiO_2 nanoparticles increases nucleation rate during C_3S hydration.

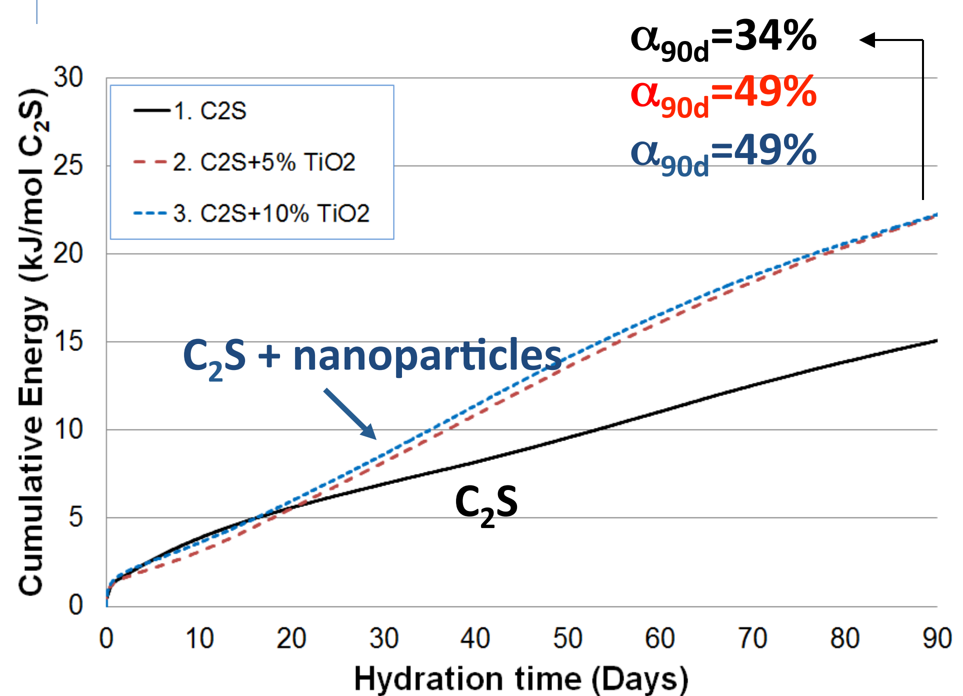
B.Y. Lee and K.E. Kurtis, *J.Am. Cer. Soc.*, Oct 2010.

Effect on Hydration: C_2S

What are the effects of nanoparticles additions to cements?



- $Acceleration: ~20 days with 5 or 10% TiO_2$
- ~45% increase in degree of hydration, α, at 90 d



By accelerating hydration, reduction in clinker content or increases in belite content are possible pathways to increased sustainability with nanoparticles.

B.Y. Lee and K.E. Kurtis, *J.Am. Cer. Soc*, Jan, 2012.

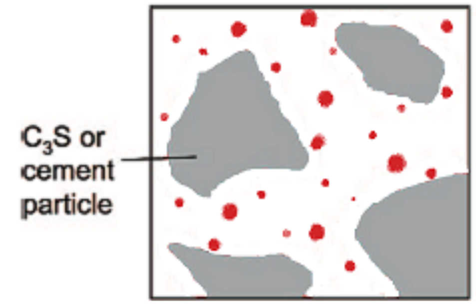
Effect on Hydration: Modeling

- Avrami model [1]

  New phase is nucleated by germ nuclei and the grain centers of the new p hase are randomly distributed.

$$R = Ank_{avr}^{n}(t-t_0)^{n-1}\exp\left(-\left[k_{avr}(t-t_0)\right]^{n}\right)$$

A : normalization constant♪
K_{avr} : effective rate constant♪
t_0 : delayed time until start of c♪



- Boundary nucleation and growth model (BNG model)[2,3]

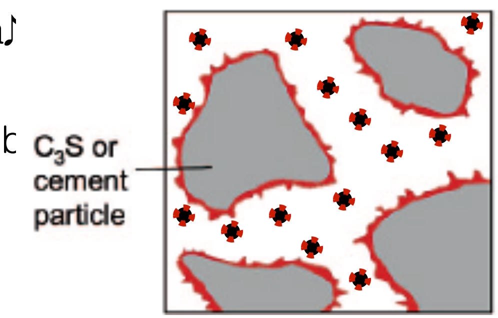
  Nucleation is favored on grain boundaries. Accounts for surface area.

$$Rate = A \cdot \frac{dX}{dt}$$

$$k_B = \left(I_B O_v^B\right)^{1/4} G^{3/4}$$

$$k_G = O_v^B G$$

O_v^B : total area of grain boundary per unit volume♪
G : linear growth rate♪
Y^e : extended area fraction of the intersection between t he plane and grains♪
k_B :the rate at which the nucleated boundary area♪ transforms♪
k_G :the rate at which the non−nucleated "grains" b en the boundaries transform♪

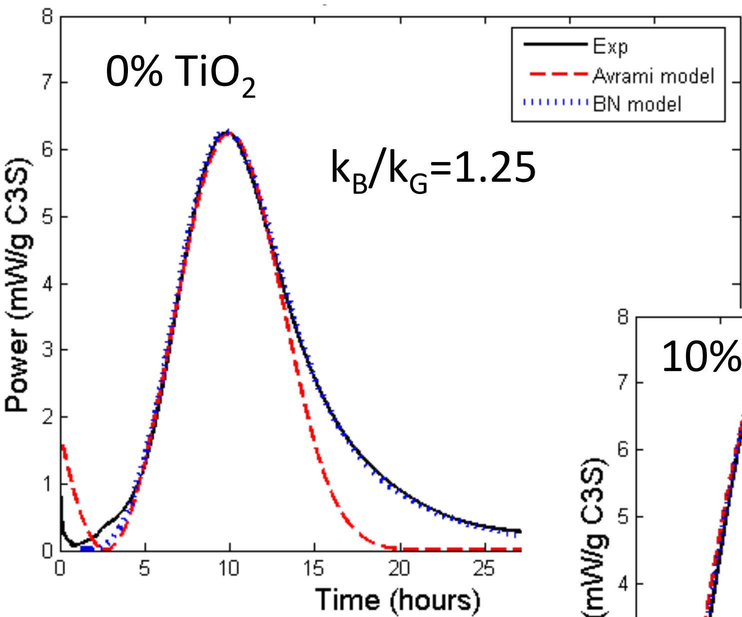


Hypothesis: Higher degree of hydration due to additional surface area provided by TiO_2 nanoparticles

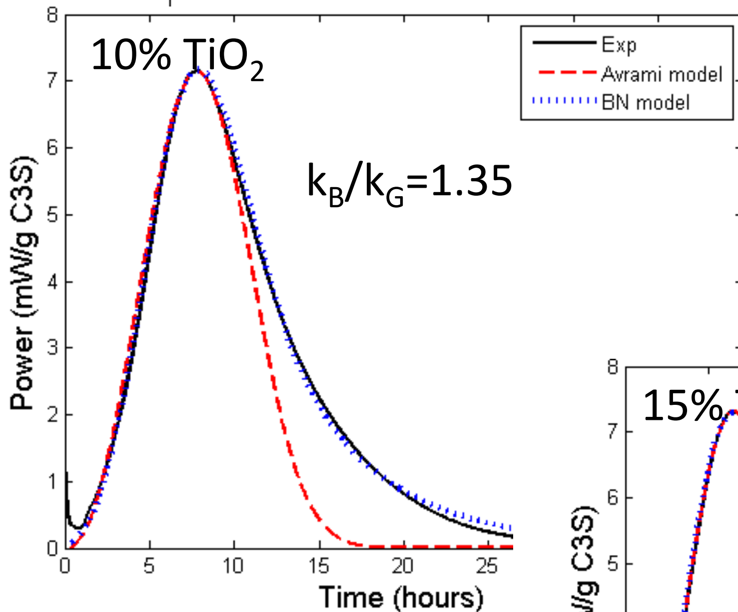
1.Avrami, Journal Of Chemical Physics, 1939,1940,1941
2.Cahn, Acta Metallurgica, 1956. **4**(5): p. 449-459.
3.J. J. Thomas and H. M. Jennings, Chem. Mater., 11, 1907-14 (1999).

Image adapted from Thomas, J. Phys. Chem., 2009.

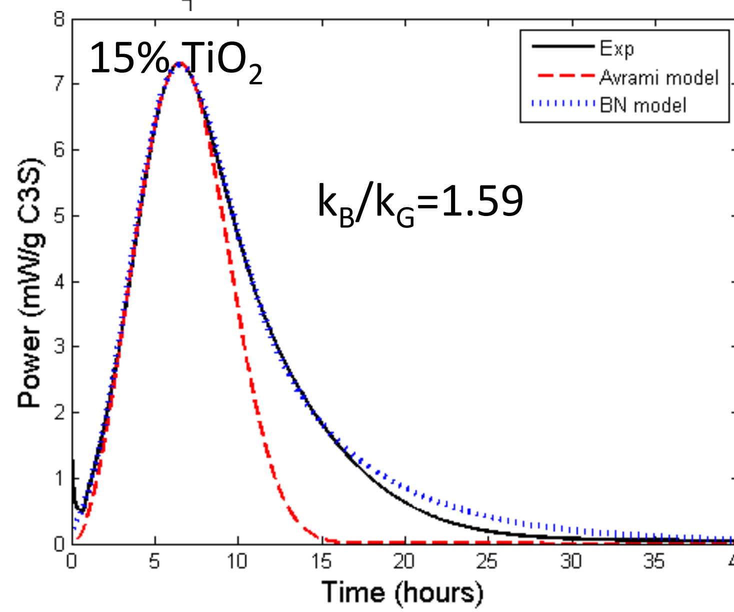
Effect on Hydration: Modeling C_3S Hydration



- For all cases BNG model gives a better fit than Avrami model



- k_B/k_G increases with increasing TiO_2 addition, suggesting that increased hydration results from boundary nucleation effects.



Supports hypothesis that nucleation is spatially nonrandom and is likely related to the surface area of the solid phases (C_3S and TiO_2 nanoparticles) available for product

B.Y. Lee and K.E. Kurtis, *J.Am. Cer. Soc.*, Oct 2010.

Preliminary Conclusions

How do TiO_2 nanoparticles affect portland cement hydration, if at all?

- TiO_2 nanoparticles accelerate early cement hydration:
  - Acceleration of C_3S hydration supported by BNG modeling, supports mechanism associated with increase in nucleation rate due to high surface area nanoparticles.
  - Accelerated C_2S hydration suggests potential for further optimizing the performance of lower-CO_2 and lower-embodied-energy cement compositions containing higher quantities of belite (e.g., 3rd series cements).

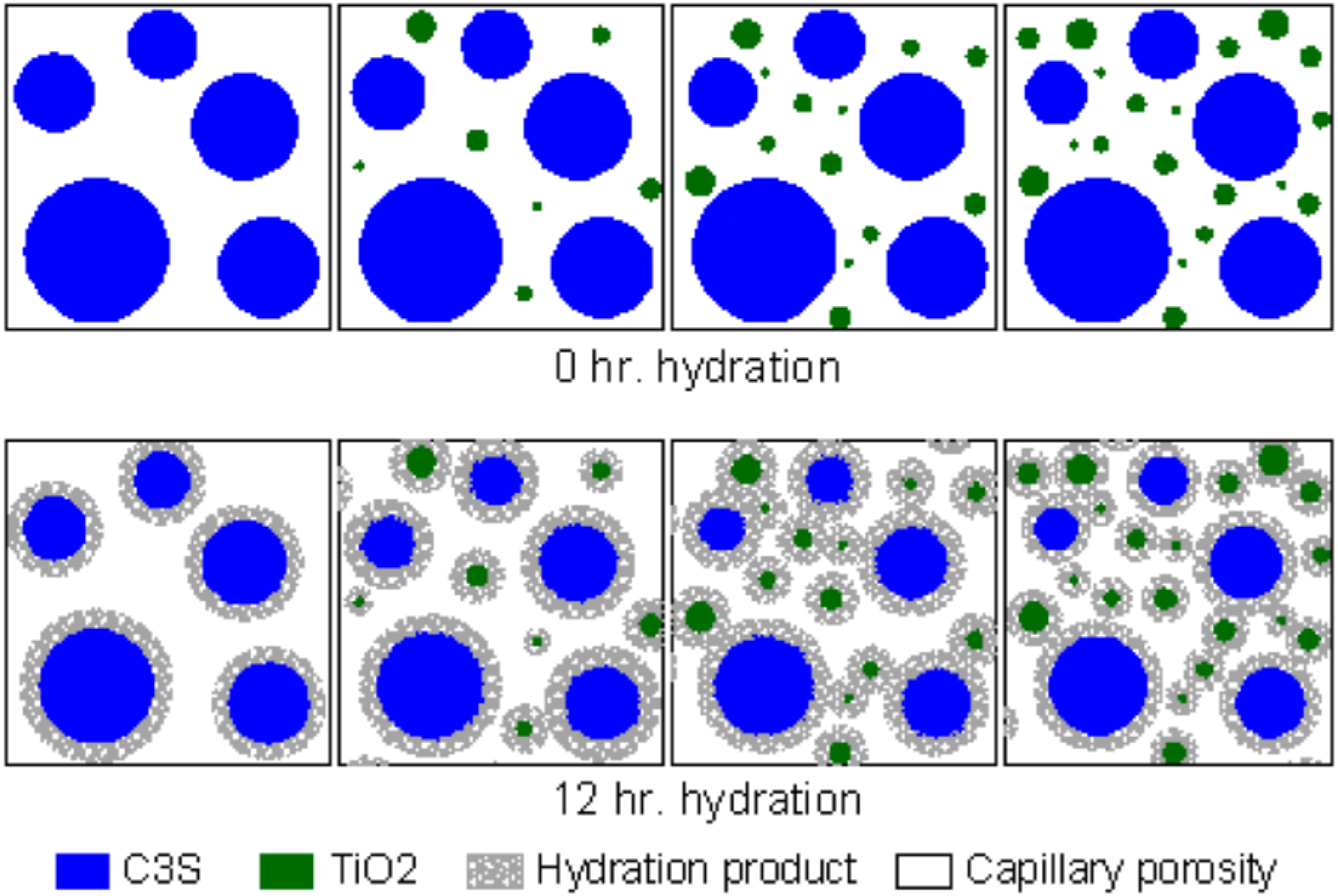
Research Questions

Way back in 2008, we asked some questions:

- How do TiO_2 nanoparticles affect portland cement hydration, if at all?
- Are the structure and properties of the cementitious host affected by the presence of TiO_2 nanoparticles?
- How effective is nanostructured TiO_2 in NOx binding on concrete surfaces?
- How does TiO_2 –nanoparticle concrete fit within the context of sustainable development?

Effect on Structure

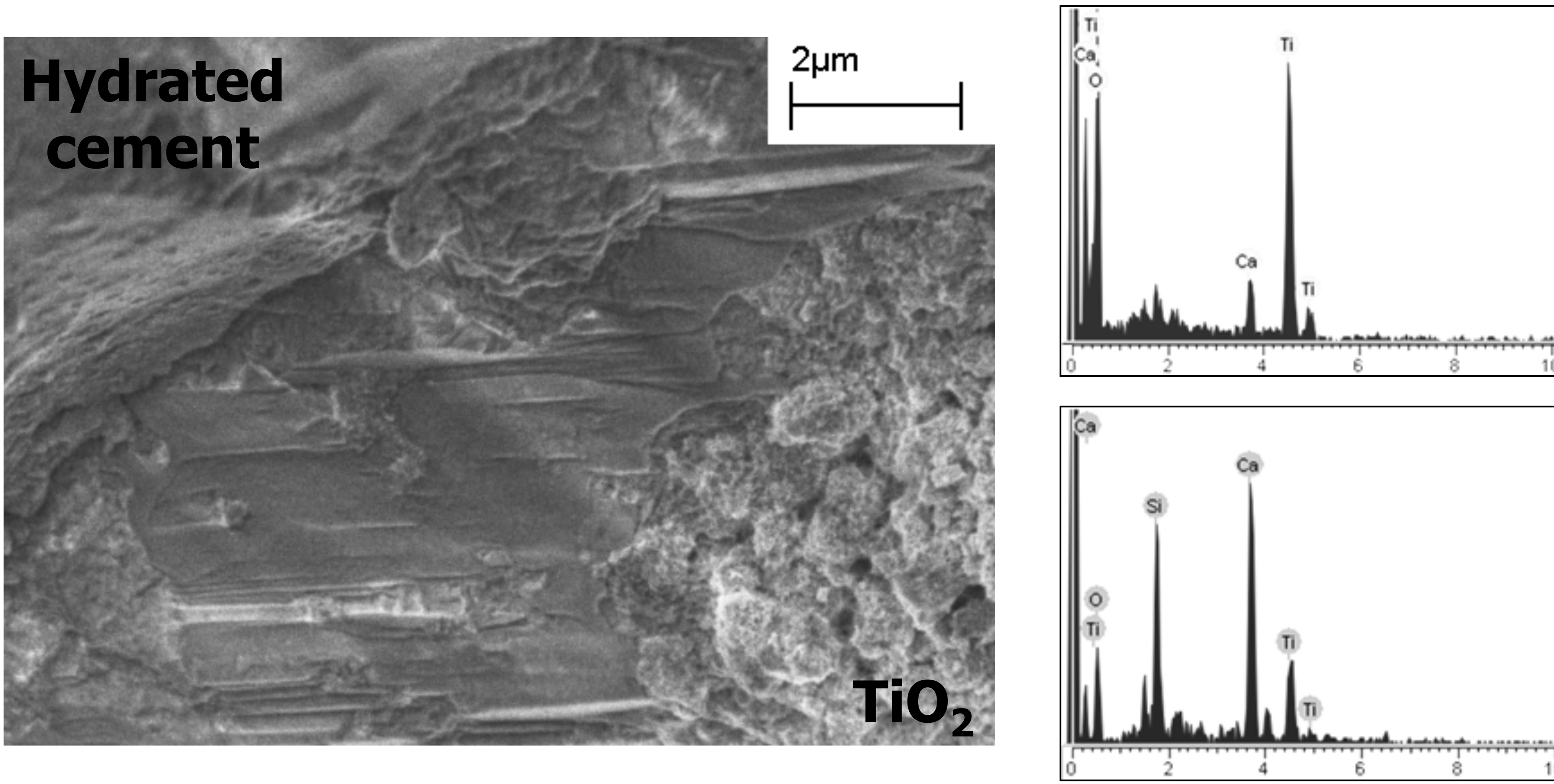
BNG model suggests reduction in capillary porosity with nanoparticle nucleation



0%, α=37% 5%, α=42% 10%, α=50% 15%, α=54%

Effect on Structure

- Denser hydration product structure observed near TiO_2 particles than those observed at distance from TiO_2



SEM image and EDS spectra at interface of TiO_2 and cement paste

Effect on Structure

Specific surface area analysis:

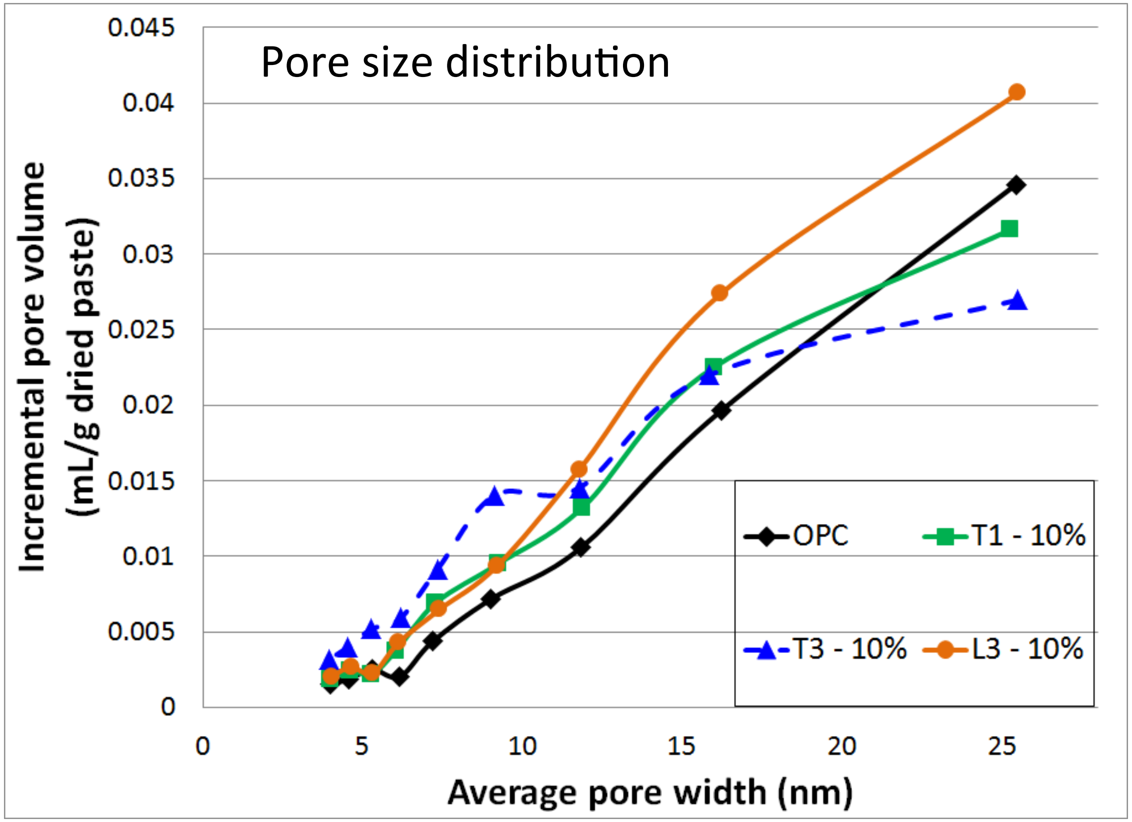
	OPC	T1 - 10%	T3 - 10%
BET surface area (m^2/g)	21.93	25.77	33.10
BJH desorption pore volume (cm^3/g)	0.088	0.099	0.115
BJH desorption average pore width (nm)	11.44	10.86	8.77

- Compared to ordinary pastes (OPC), nanoparticle pastes had a higher surface area and pore volume and a smaller average pore size
  - Fine fillers could encourage the formation of high surface area C-S-H[1]

1. Juenger and Jennings, *CCR, 2001*

Jayapalan, Lee, Kurtis, *CCC*, 2013.

Effect on Structure



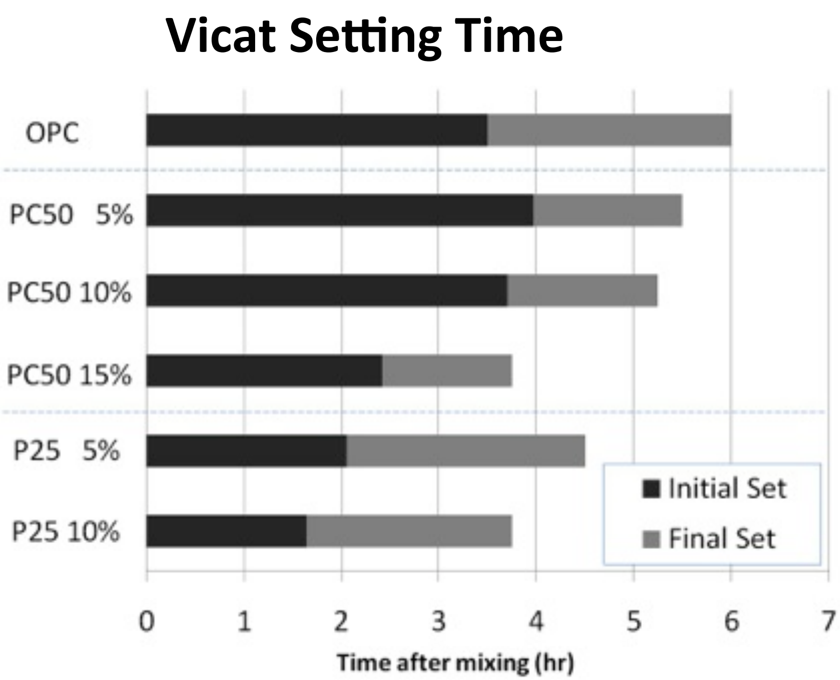
- Compared to OPC, the TiO_2 nanoparticle pastes had higher volume of small (<4nm) and medium sized (4-20nm) pores and a smaller volume of larger pores (>20nm)

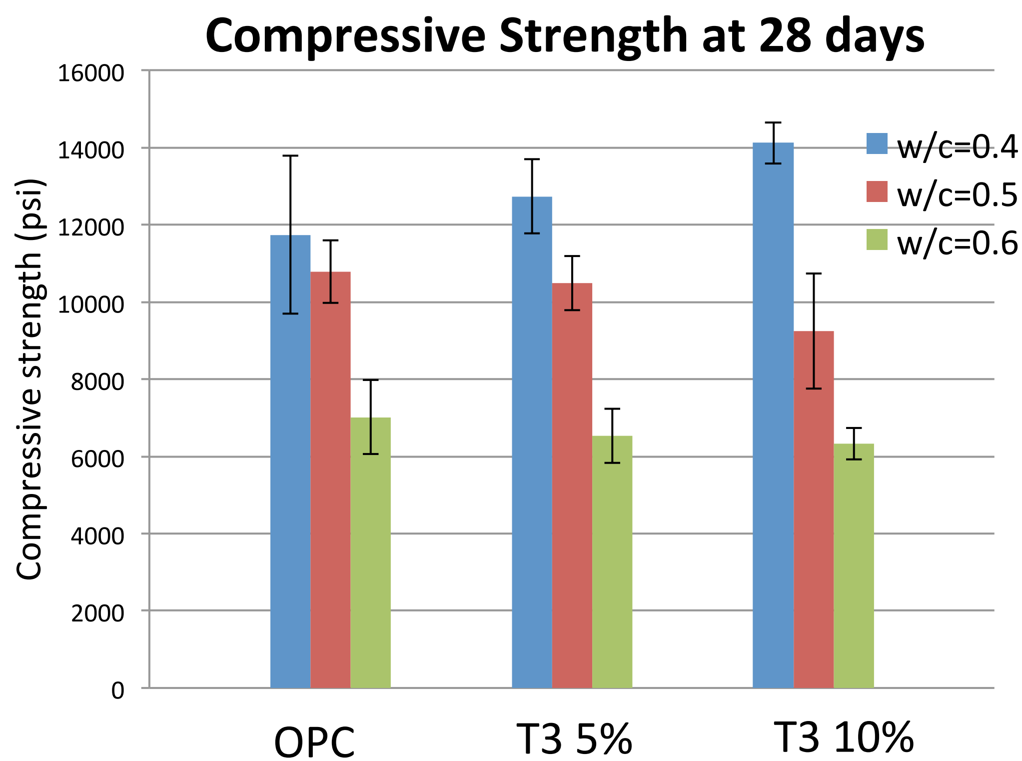
- Due to nucleation and growth effects, nanoparticles (T3, T1) may refine capillary porosity, with the finest, most dispersible TiO_2 exhibiting greatest reduction in pore size.
- Further research is needed to better understand relationship between changes in pore structure, transport properties and durability

Jayapalan, Lee, Kurtis, *CCC*, 2013.

Effect on Properties

- Shortened setting time
- Retention and slight increases in strength, at lower w/c, despite reduction in cement content





Preliminary Conclusions

Are the structure and properties of the cementitious host affected by the presence of TiO_2 nanoparticles?

- Despite greater porosity, pore structure refined (smaller pores) while reducing clinker content.
- Strength maintained, while reducing clinker fraction.

Research Questions

Way back in 2008, we asked some questions:

- How do TiO_2 nanoparticles affect portland cement hydration, if at all?
- Are the structure and properties of the cementitious host affected by the presence of TiO_2 nanoparticles?
- How effective is nanostructured TiO_2 in NOx binding on concrete surfaces?
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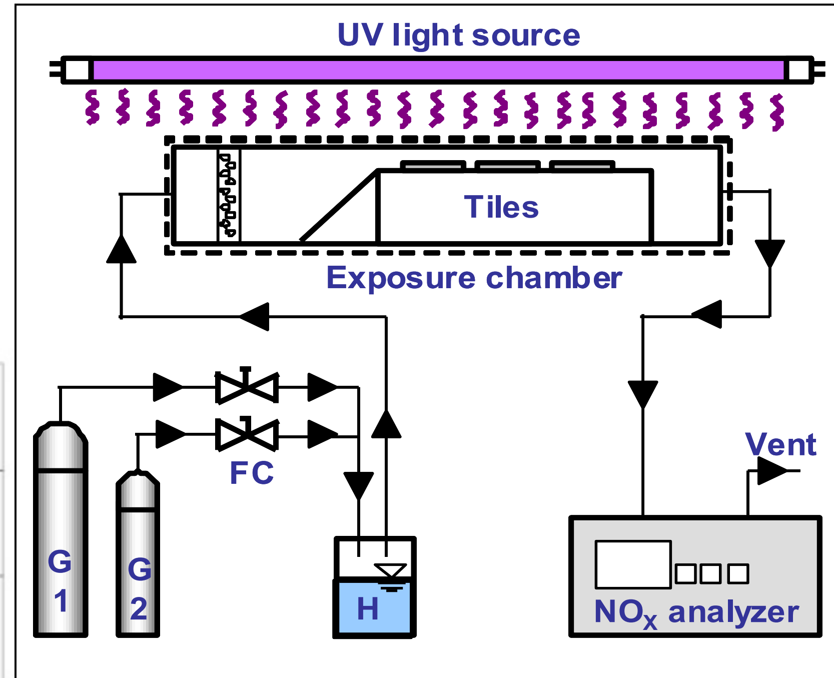
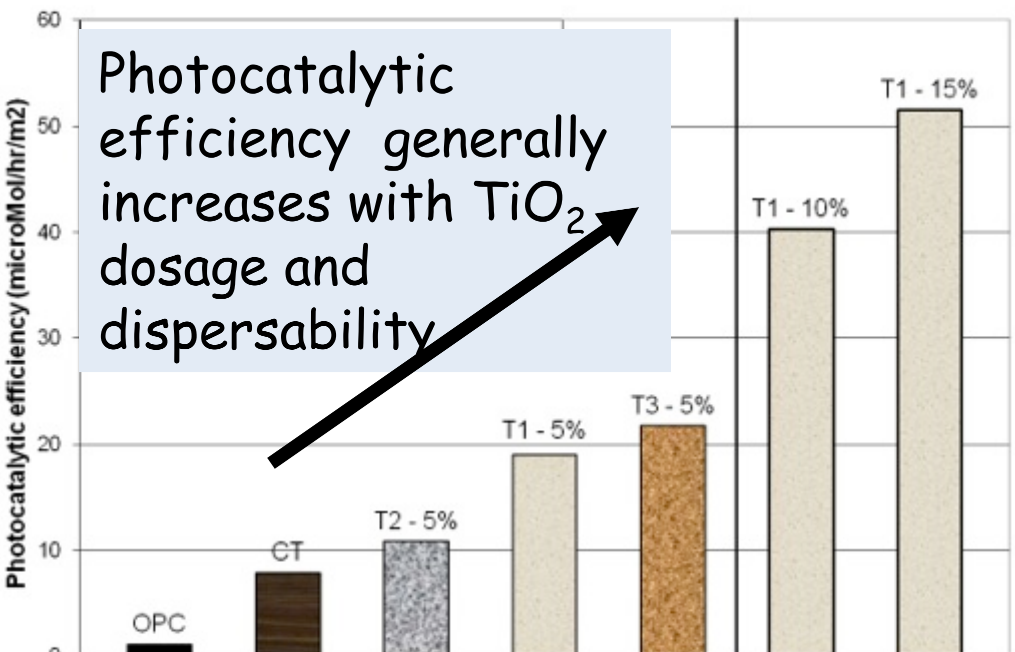
Nitrogen Oxide (NO) Binding

Influence of TiO_2 particle addition rate on photocatalytic efficiency, during standard NO testing.



G1 – zero air source, G2 – NO source, FC – digital mass-flow controllers, H – humidifying and mixing chamber

Photocatalytic efficiency generally increases with TiO_2 dosage and dispersability

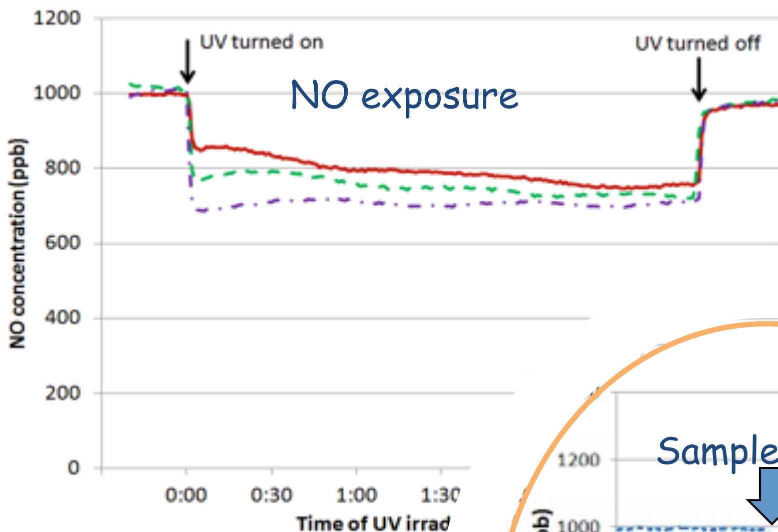


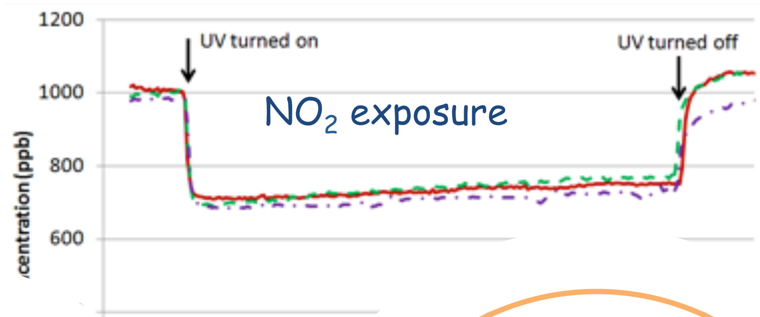
$$PEF = \frac{f}{22.4 \cdot A \cdot T}\left\{\int_0^T \left([NO_X]_{in} - [NO_X]_{out}\right) dt\right\}$$

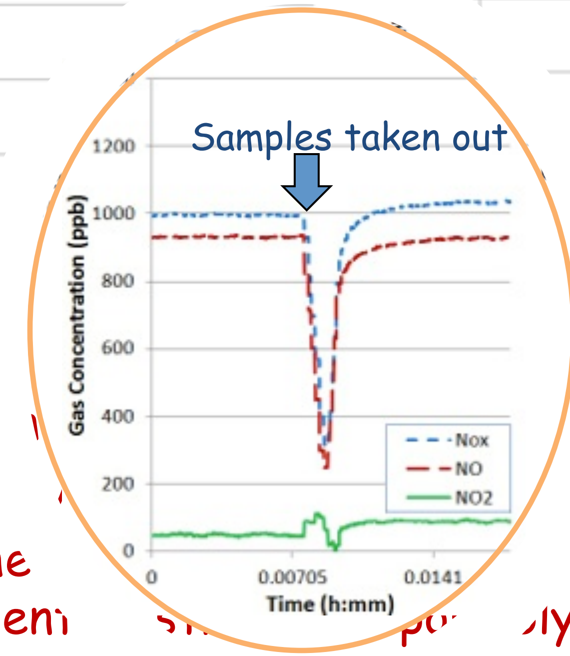
Jayapalan, Bergin, Kurtis, in review, *ACI Materials*.

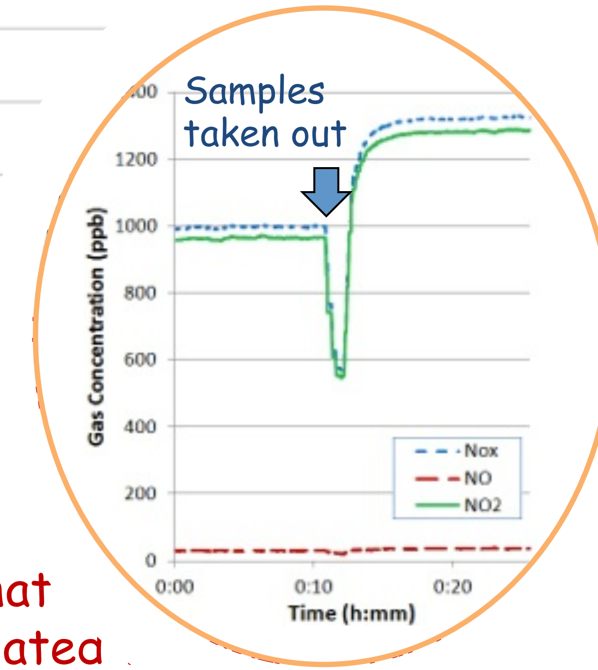
Photocatalytically-induced Binding of NO vs. NO_2

- w/b=0.4, 0.5, 0.6 @ 5% TiO_2 wt. replacement of cement
- Photocatalytic reactivity = percent drop of gas concentration







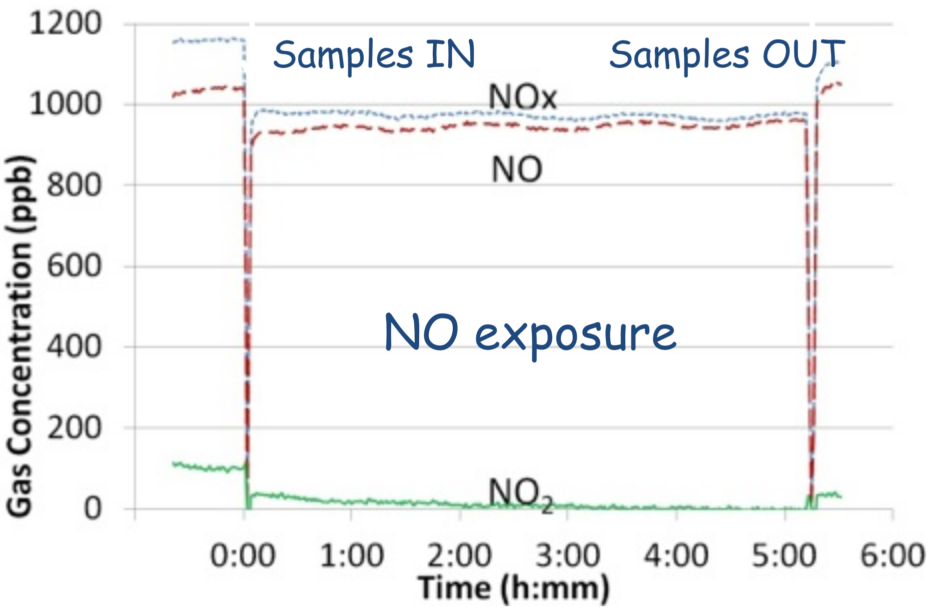


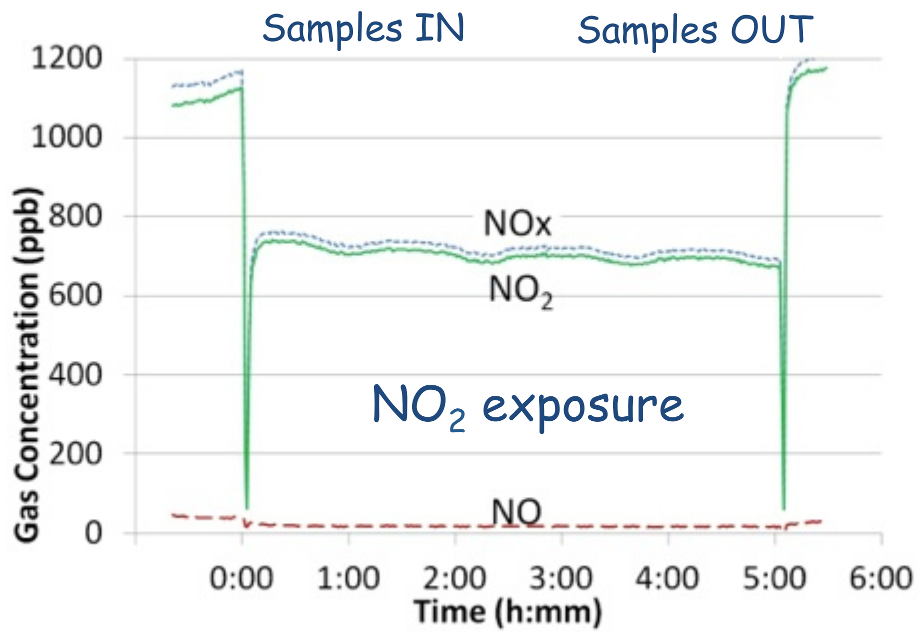
- Similar amounts of N
- NO exposure: ↑ w/b
  ↑ oxidation at early
- NO_2 exposure: no obs
- It is proposed that the … that efficiency is independent … related … dipole moment.

Lee, Jayapalan, Bergin, Kurtis, *Cem. Concr. Res.*, in re-review.

Ordinary Binding of NO vs. NO_2

- UV light not used
- w/b=0.6 @ 10% TiO_2 wt. replacement of cement
- Samples exposed in ‘wet’ conditions

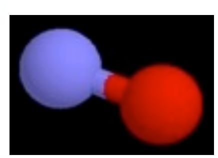




- Greater amounts of NO_2 are bound within cementitious materials than NO gas → may be due to polarity

NO_2: 0.316D – polar

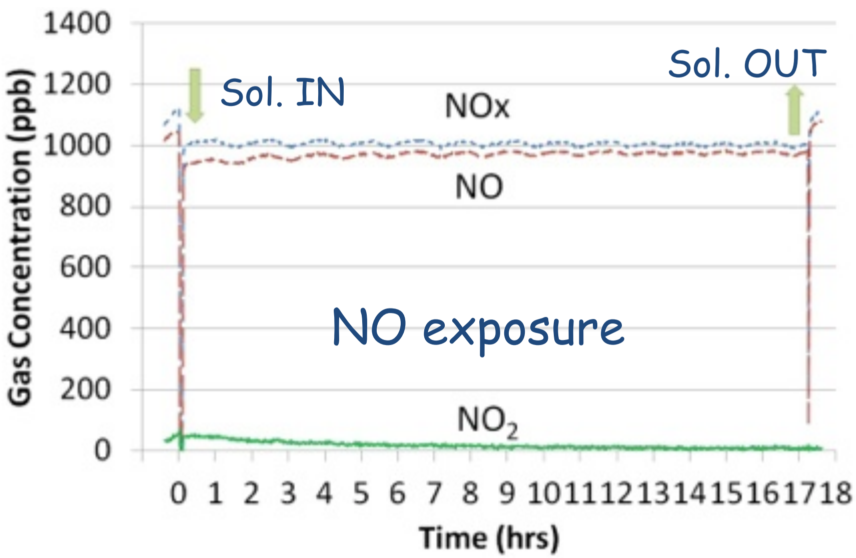
NO: 0.157D – almost non-polar

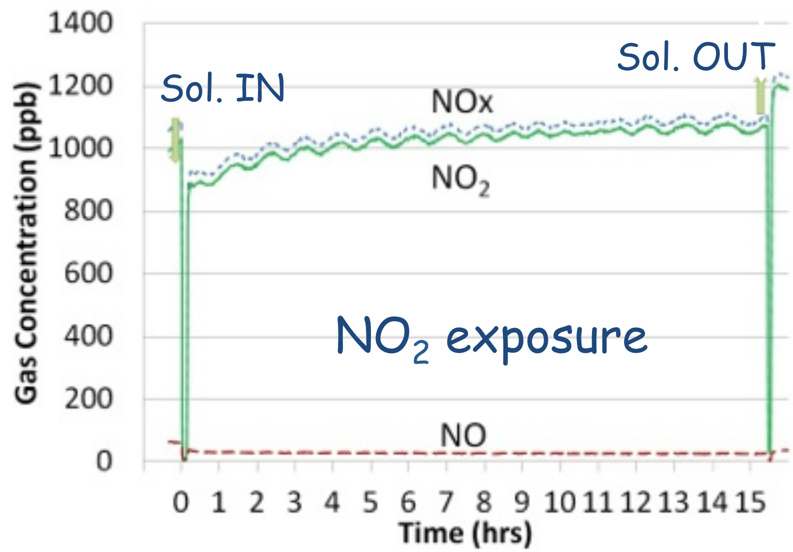


Lee, Jayapalan, Bergin, Kurtis, *Cem. Concr. Res.,* in re-review.

Ordinary Binding of NO vs. NO_2: Pore Solution

- UV light not used.
- Pore solution used in place of cement samples.
- Synthetic pore solution: saturated $Ca(OH)_2$ + 0.7M NaOH





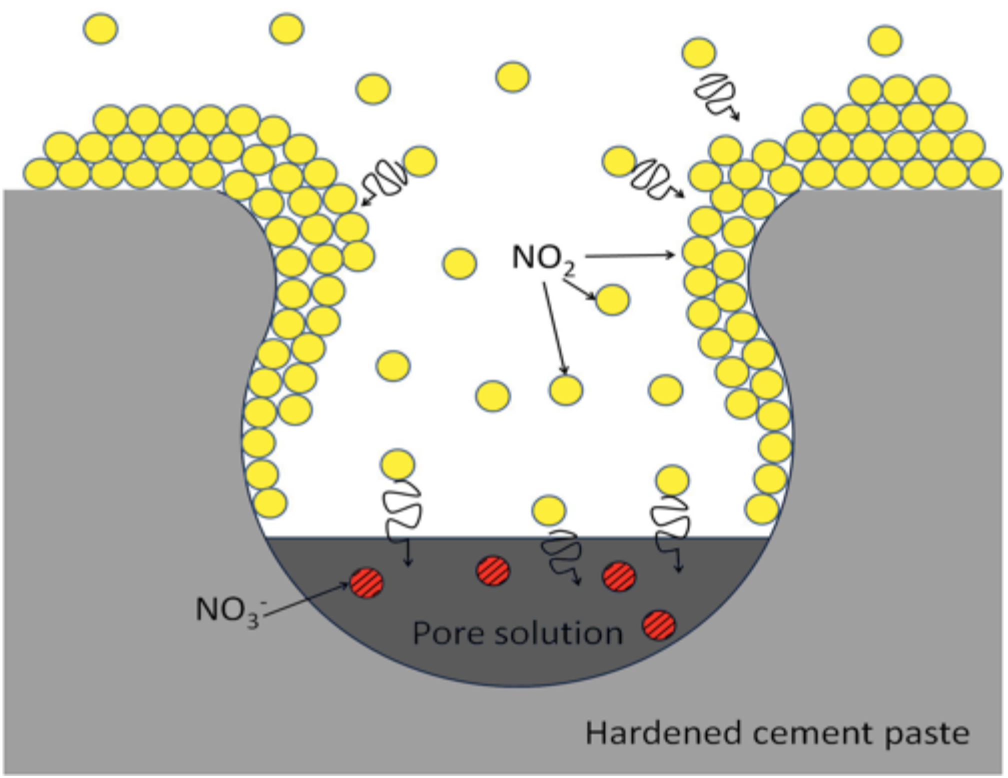
- NO and NO_2 can be absorbed in cement pore solution, consistently for 15hrs.
- Pore solution may play a lesser role in NOx binding.

Similarities in binding of NO and NO_2 in pore solution suggest that NO_2 has a greater affinity to <u>solids</u> in hydrated cement paste than NO.

Lee, Jayapalan, Bergin, Kurtis, submitted to *Cem. Concr. Res.*

Ordinary Binding of NO vs. NO_2

- It is proposed that binding of NO and NO_2 can occur independently of photocatalysis in cementitious materials
- Potentially alters perceptions of associated environmental impact of cementitious materials



Lee, Jayapalan, Bergin, Kurtis, *Cem. Concr. Res.*, in re-review.

Proposed NO_2 binding mechanisms:

- NO_2 is preferably adsorbed on hydration products than absorbed in pore solution
- Stacked in layers possible due to its high dipole moment
- Some absorption in pore solution

Preliminary Conclusions

How effective is nanostructured TiO_2 in NOx binding on concrete surfaces?

- NOx binding increases with increasing TiO_2 use rate and dispersion.
- Long-term NOx binding generally independent of w/b
  - Some short-term effects were observed for NO, with higher w/b (higher porosity) leading to greater binding efficiency
- Greater affinity for NO_2 binding was attributed to greater polarity of NO_2 vs NO
  - NOx binding, and binding of NO_2 in particular, can occur in the absence of photocatalysis

Research Questions

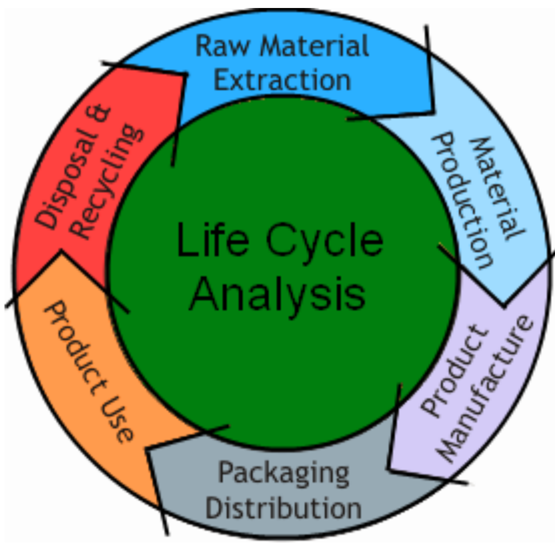
Way back in 2008, we asked some questions:

- How do TiO_2 nanoparticles affect portland cement hydration, if at all?
- Are the structure and properties of the cementitious host affected by the presence of TiO_2 nanoparticles?
- How effective is nanostructured TiO_2 in NOx binding on concrete surfaces?
- Is there any potential for damage to the cementitious host during photocatalysis?
- How does TiO_2-nanoparticle concrete fit within the context of sustainable development?

Sustainability: Life Cycle Analysis

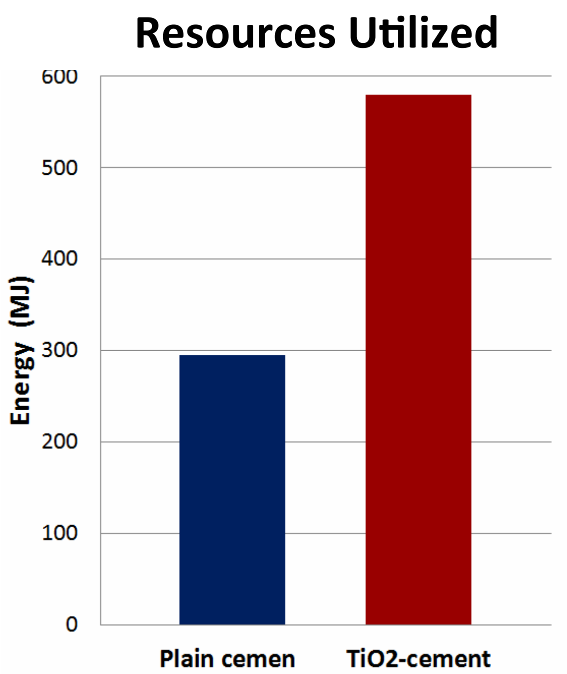
- Life Cycle Analysis (LCA) analyzes environmental impact of a product
  - Considers all energy and emissions from raw material production stage through recycling or end-of-life disposal (cradle-to-grave approach)

- Useful technique for the <u>comparison</u> of environmental impact of different materials
  - w/s=0.50 , 5% filler replacement
  - 1000kg of the cementitious materials was used
  - NOx binding capability of TiO_2-cement included

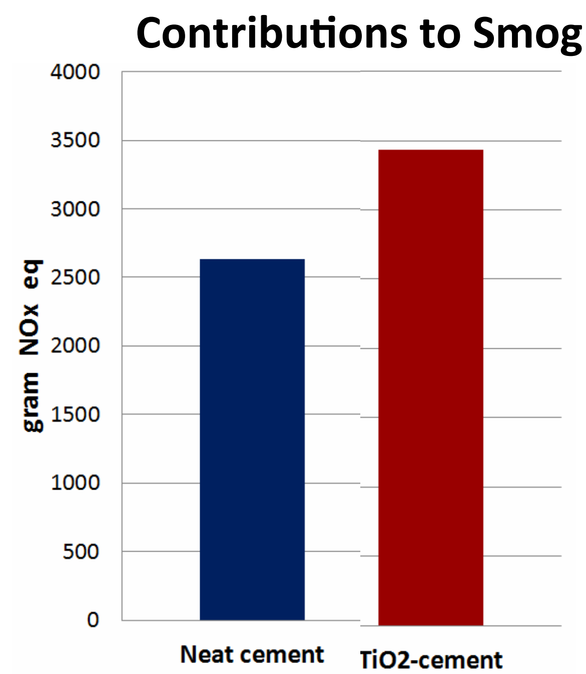


- Software: *SimaPro* LCA analysis
- Impact assessment techniques: *EcoIndicator* and *BEES*

Life Cycle Analysis



Resources utilized by OPC and TiO_2-cements



NOx emissions by OPC and TiO_2-cements

- 5% TiO_2-cement mixes have a considerably higher environmental "cost" than ordinary concrete

Jayapalan, Lee, Kurtis, *CCC*, 2013..

Life Cycle Analysis: Offset of NOx

Can photocatalysis in the presence of TiO_2, sunlight and water offset initial (embodied) NOx emissions by TiO_2-cement mixes?

Conditions in Atlanta, USA were considered for calculations

- 17ppb average NOx concentration
- 7.25 hours average daily sunshine

Days for photocatalysis by TiO_2-cement surface to offset initial NOx emissions

TiO_2-cement layer thickness	Number of days to offset embodied NO_x
5 mm	776 days
10 mm	1553 days

- Higher initial emissions by TiO_2-cement systems offset by photocatalysis in 2.12 years for 5mm thick layer
- In the long term, TiO_2-modified cements could be considered as a sustainable construction product

Jayapalan, Lee, Kurtis, *CCC*, 2013..

Conclusions

How does TiO_2 –nanoparticle concrete fit within the context of sustainable development?

- Nanoparticles stimulate cement hydration, due to increased nucleation
  - Reduced clinker fractions
  - Increased C_2S contents
  - Maintain setting time, strength development rate

Lower embodied energy, emissions associated with cement manufacture

- Nanoparticles densify paste structure
  - Reduced pore size, increased pore volume (presumably due to a greater amount of C-S-H formed)
  - Could improve durability, but further research is needed to verify impact on transport properties

Increased durability would also support sustainability.

Conclusions

How does TiO_2 –nanoparticle concrete fit within the context of sustainable development?

- Cementitious materials capable of measurable NOx binding, independent of the presence of photocatalysts.

  → Could be optimized to further support sustainability.

- Likely that photocatalysis enhances NOx binding capabilities
  - TiO_2 nanoparticles do provide additional benefit, but at an increased initial environmental cost
  - Initial NOx "cost" can be offset as early as ~2 years in TiO_2-cement coatings

- Photocatalysis also provides self-cleaning, biocidal, and VOC binding capabilities, not found with ordinary cementitious materials

Acknowledgments

Huge gratitude to **Dr. Amal Jayapalan** and **Dr. Bo Yeon Lee** for their tireless efforts and insights.

We are grateful to Prof. Mike Bergin at Georgia Tech for his assistance in the NOx exposure studies and to Prof. John Crittenden's group at Georgia Tech for their training and consultation on the LCA.

Questions?

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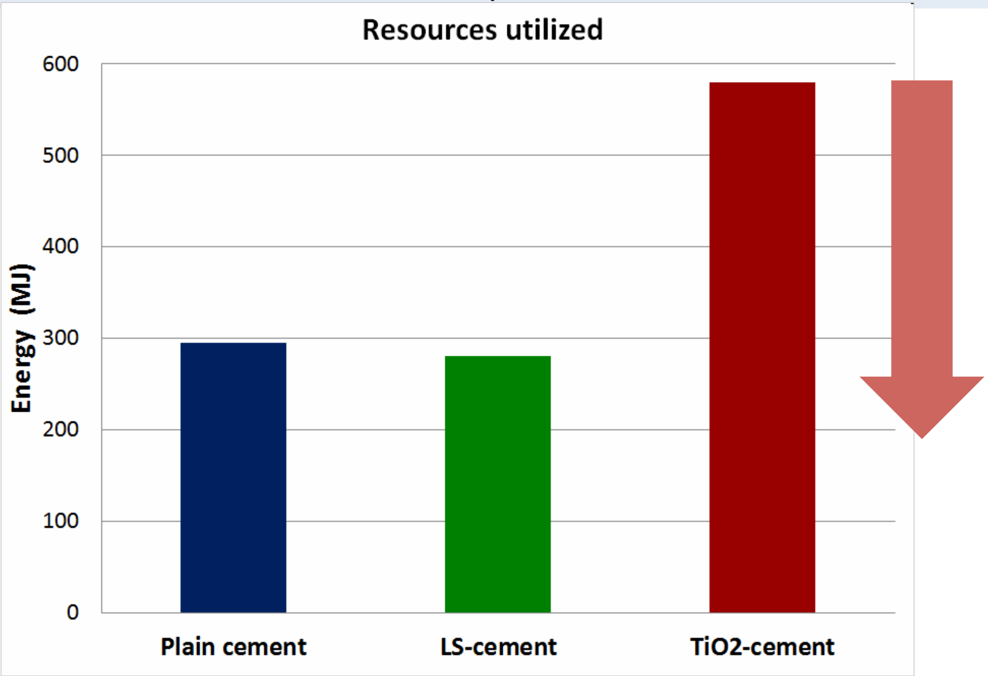
National Science Foundation
WHERE DISCOVERIES BEGIN

Georgia Institute of Technology

Seems nanoparticles can *potentially* contribute to sustainability in cement and concrete, but we are not quite there… yet.

Further Research: Optimizing Fillers

Identification of an "optimum" inert filler material or a mixture of filler materials from both particle size and embodied energy perspective could be a pathway to enhance sustainability of cementitious materials

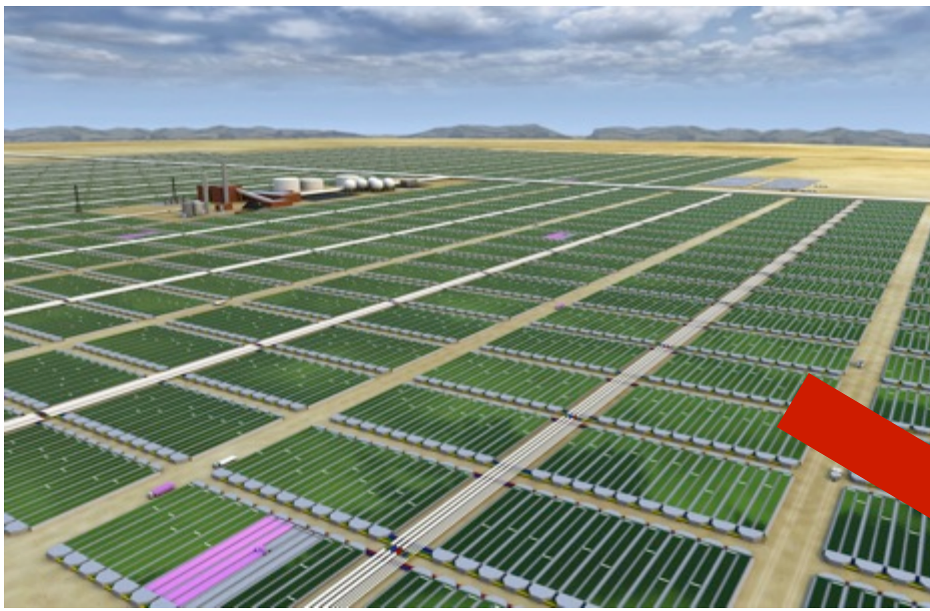


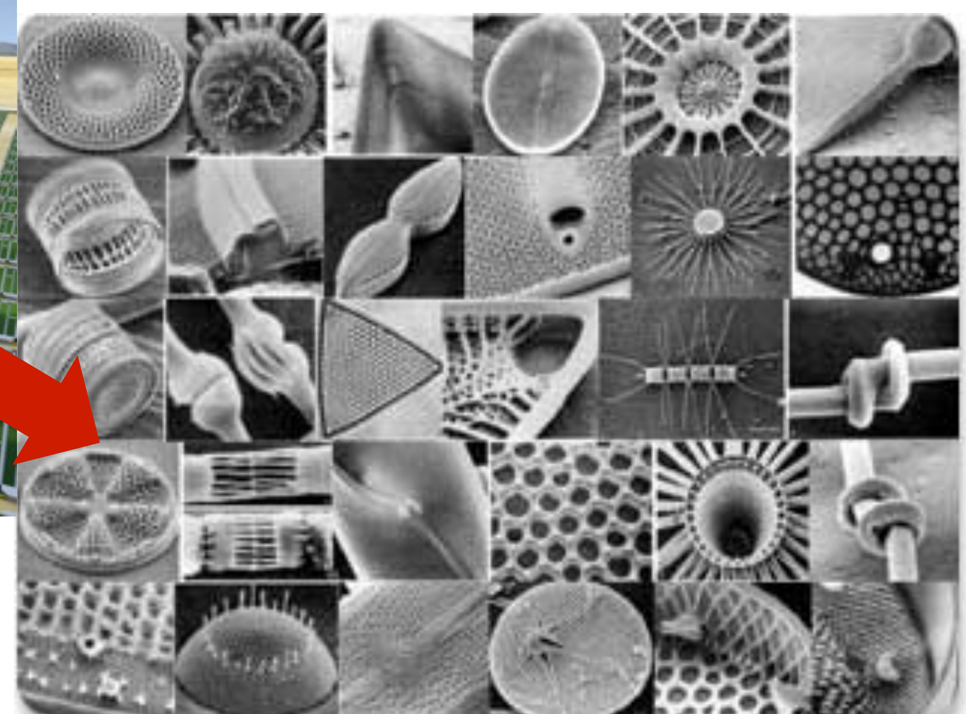
Resources utilized by OPC and blended cements

- Lower embodied-energy nanoparticles are needed
    - Innovations in lower-energy production of TiO_2 nanoparticles
    - Blending of filler nano and microparticles
    - Blending of filler nanoparticles and SCMs
    - Other…

Further Research: Optimizing Fillers

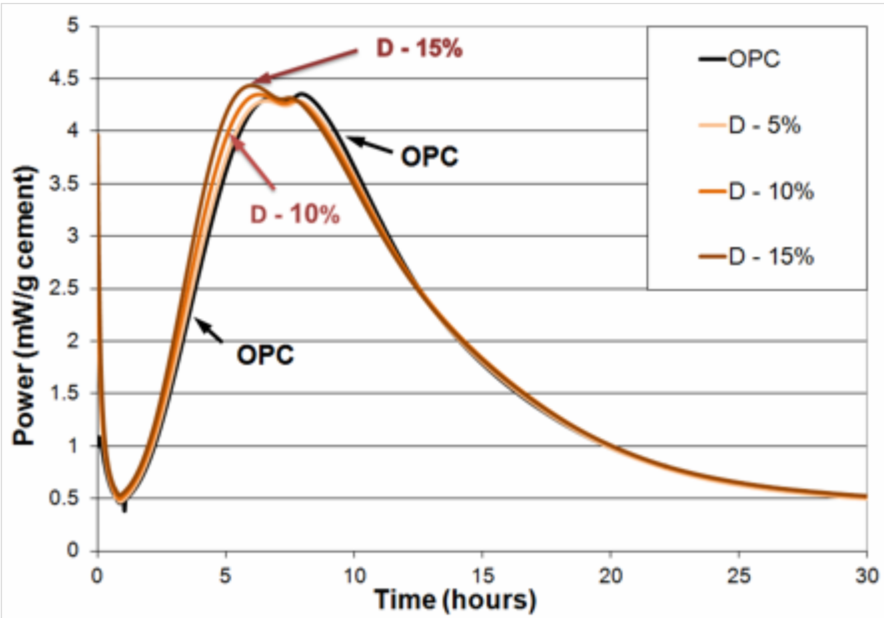
- Natural materials or industrial by-products could reduce environmental impact and economic cost
- Diatomaceous earth (DE) – silicon rich bio-energy by-product - could be an alternative source of "nanoparticles"



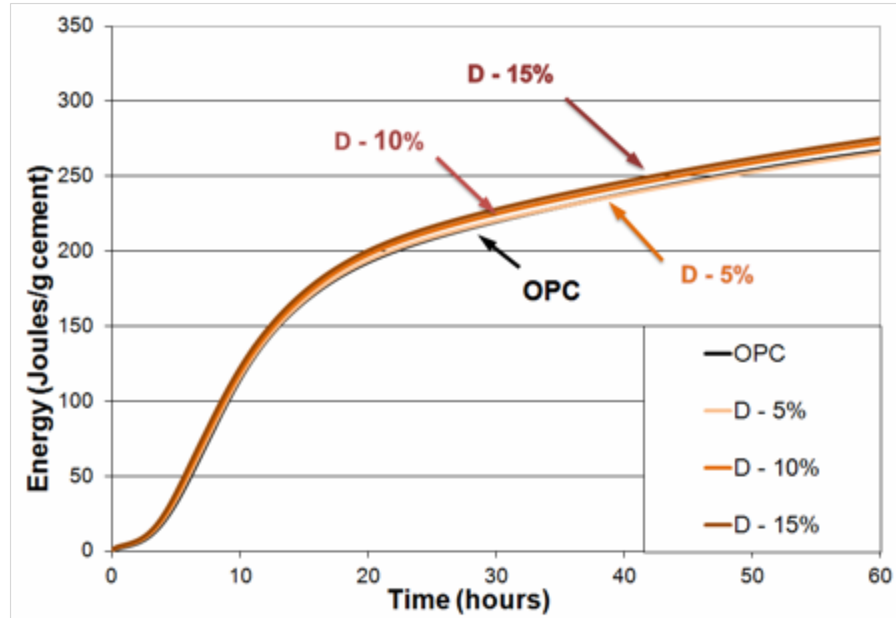


- Greengossip.com
- Center for Bio-inspired Design (CBID), Georgia Institute of Technology

Further Research: Optimizing Fillers



Rate of hydration of diatom-cement mixes



Total heat evolution of diatom-cement mixes

- Diatomaceous earth with 3μm particle size was used as a filler material for cement
- Slight increases in hydration with 10% and 15% DE

Work continues…

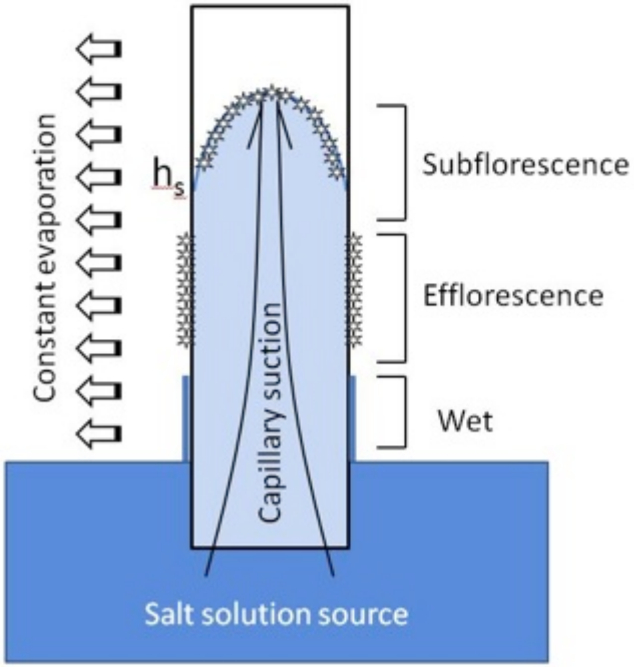
Seems nanoparticles can *potentially* contribute to sustainability in cement and concrete, but we are not quite there… yet.

Effects on Durability

- Calcium nitrate salts are used:

  - Nitrate ions (NO_3^-) from photocatalytic NOx oxidation could combine with calcium ions, forming hygroscopic calcium nitrate salts ($Ca(NO_3)_2 \cdot 4H_2O$).

- Salt crystallization study allows for examination of changes in pore structure due to nanoparticle addition on durability (relevance to sulfate attack, DEF, freeze/ thaw, etc.)



<Condition of supersaturation>

→ capillary rise and evaporation

<u>Subflorescence</u>: rate of evaporation > capillary rise

Salt crystallizes within the pores. Damage occurs.

<u>h_s</u>: rate of evaporation = capillary rise

<u>Efflorescence</u>: evaporation < capillary rise

Supersaturation reached.

Salt precipitates out on the surface

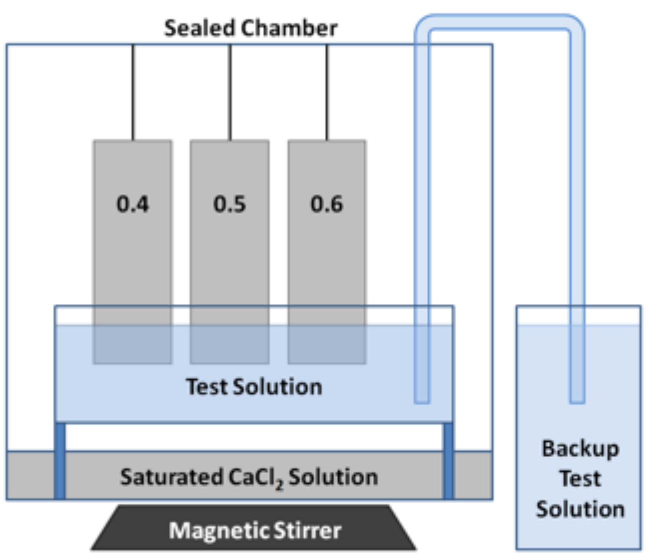
<u>Wet</u>: supersaturation not reached because the salt diffuses back towards the source.

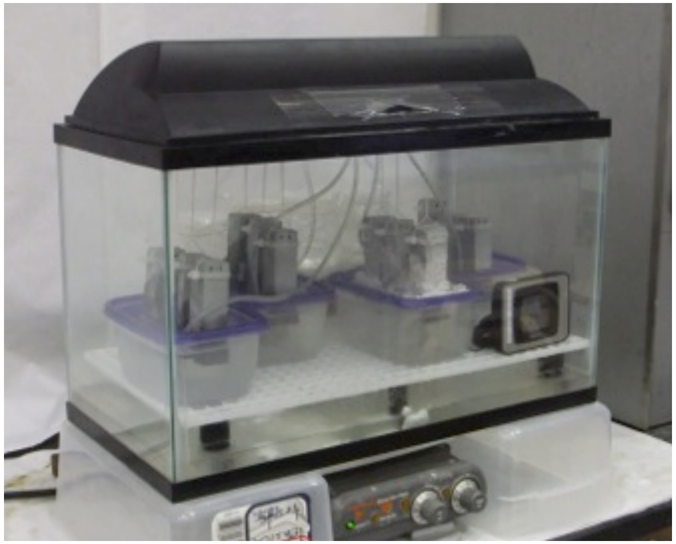
Effects on Durability

- Mortar bar samples @ w/b=0.4, 0.5, 0.6, TiO_2=0%, 5%, 10%, 15%

	0% TiO_2	5% TiO_2 sample				10% TiO_2	15% TiO_2
	$Ca(NO_3)_2$ 15%	$Ca(NO_3)_2$ 15%	$Ca(NO_3)_2$ 30%	Na_2SO_4 15%	Deionized water	$Ca(NO_3)_2$ 15%	$Ca(NO_3)_2$ 15%
0.4		O	O	O	O		
0.5	O	O	O	O	O	O	O
0.6		O	O	O	O		

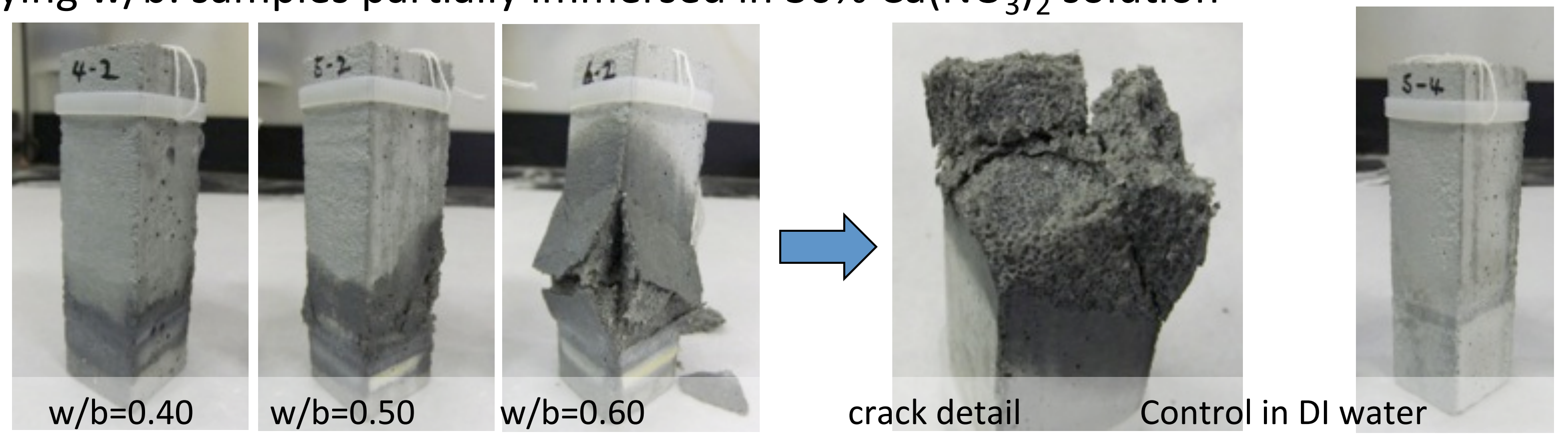
- Partially immersed in 15%, 30% $Ca(NO_3)_2$ solution
- Relative humidity=35±3% (saturated $CaCl_2$ sol.)





Effects on Durability

- Varying w/b: samples partially immersed in 30% $Ca(NO_3)_2$ solution

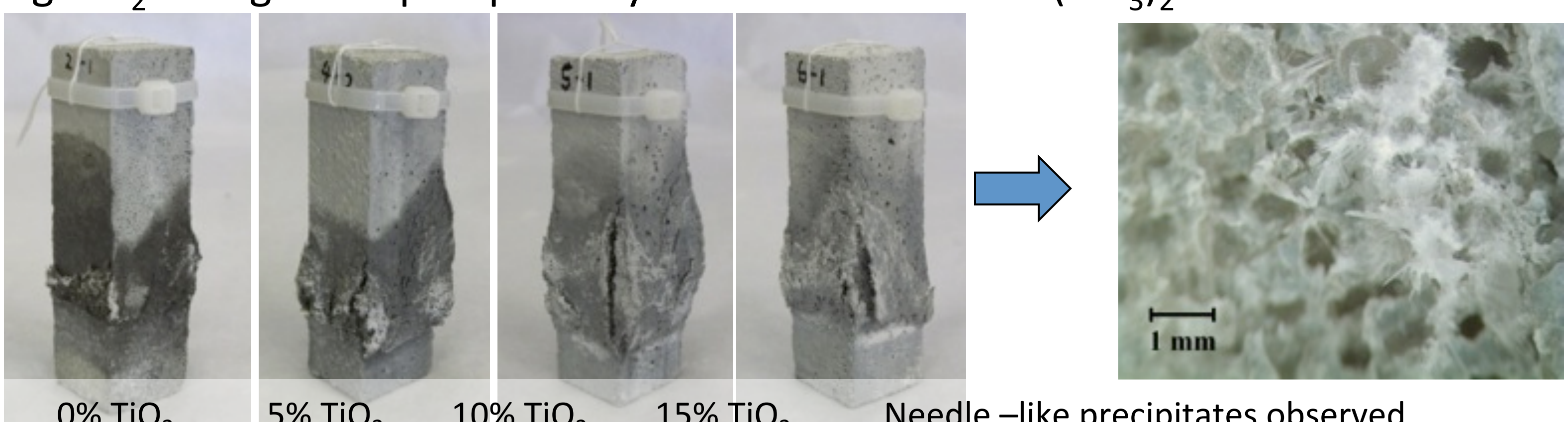


w/b=0.40 w/b=0.50 w/b=0.60 crack detail Control in DI water

Higher w/b → higher porosity, lower strength → more damage

$Ca(NO_3)_2$ salts can induce cracking and spalling to cementitious materials

- Varying TiO_2 dosage: samples partially immersed in 15% $Ca(NO_3)_2$ solution

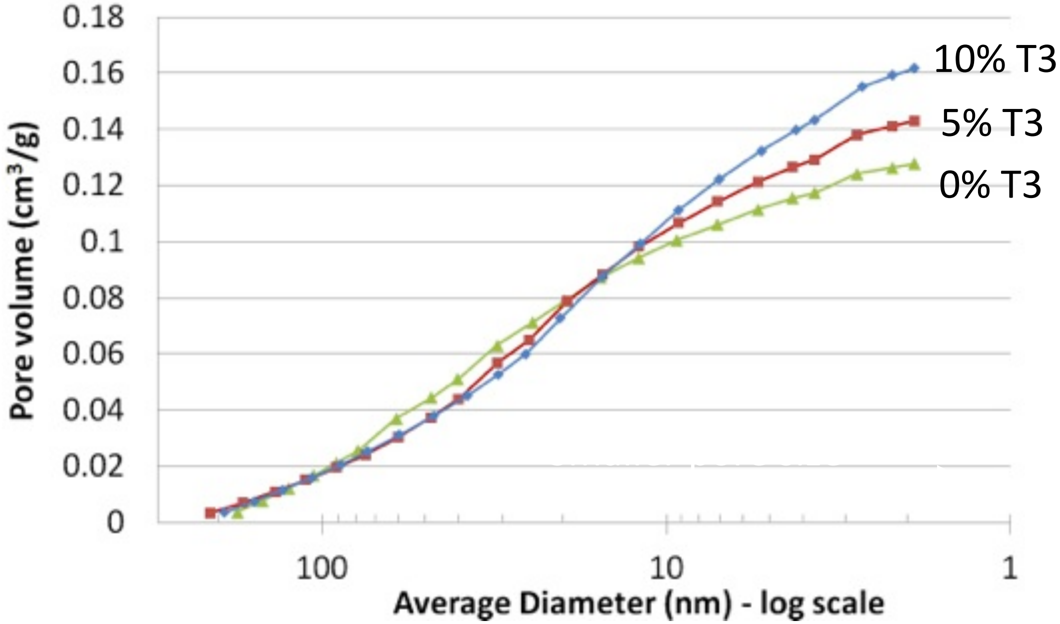


0% TiO_2 5% TiO_2 10% TiO_2 15% TiO_2 Needle –like precipitates observed

Higher TiO_2 → finer pore structure → more damage

Effects on Durability

- Cumulative pore size distribution: 7 day, w/b=0.5 in adsorption



- Higher replacement rate of TiO_2 resulted in greater pore volume and pore area at smaller pores.
- Smaller pores → greater salt crystallization pressure

$$p_w = \frac{R_g T}{V_c} \ln\left(\frac{Q^E}{Q^S}\right) = \frac{\gamma_{CL}}{r_p - \delta}$$

Suggests that addition of TiO_2 nanoparticles change microstructure.

Conclusions

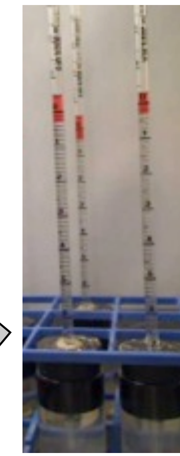
- TiO_2 nanoparticles accelerate early hydration of C_3S and C_2S by providing nucleation sites, as supported by BNG modeling.
  - Accelerated C_2S hydration suggests potential for further optimizing the performance of lower-CO_2 and lower-energy cement compositions containing belite.
  - Strength maintained and pore structure refined, while reducing clinker fraction.

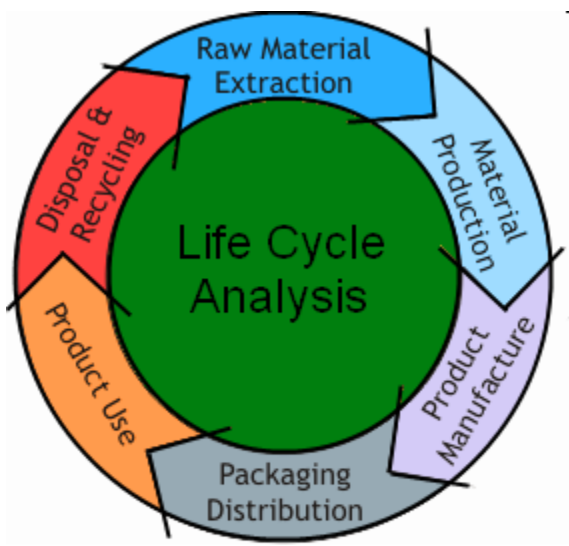
Conclusions

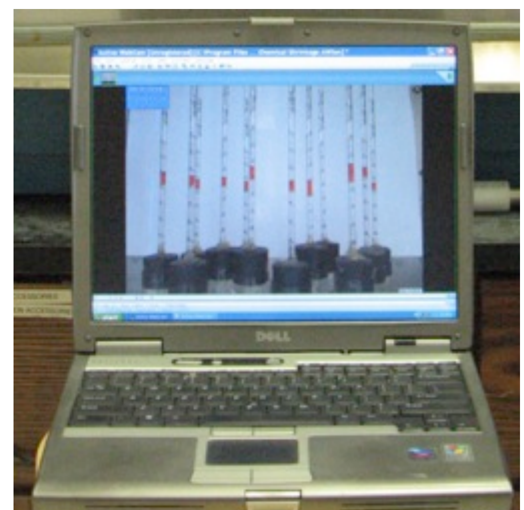
- Nanoparticles (submicron) accelerate hydration of calcium silicates, with increasing effects generally with decreasing particle size and increasing dosage rate
  - Can be used advantageously to reduce clinker content while retaining setting time and strength
  - Concomitant increases in chemical shrinkage might be mitigated by combination with microparticles, 10% dosage of ~20um
- Refinement in pore size with nanoparticle and microparticle addition
  - Further research necessary to confirm potential contributions to durability
- LCA shows that engineered nanoparticles substantially increase embodied energy when used in cements
  - Lower embodied energy nanoparticles
  - Combination of nanoparticles and lower embodied energy inert and/or pozzolanic microparticles

Research Approach

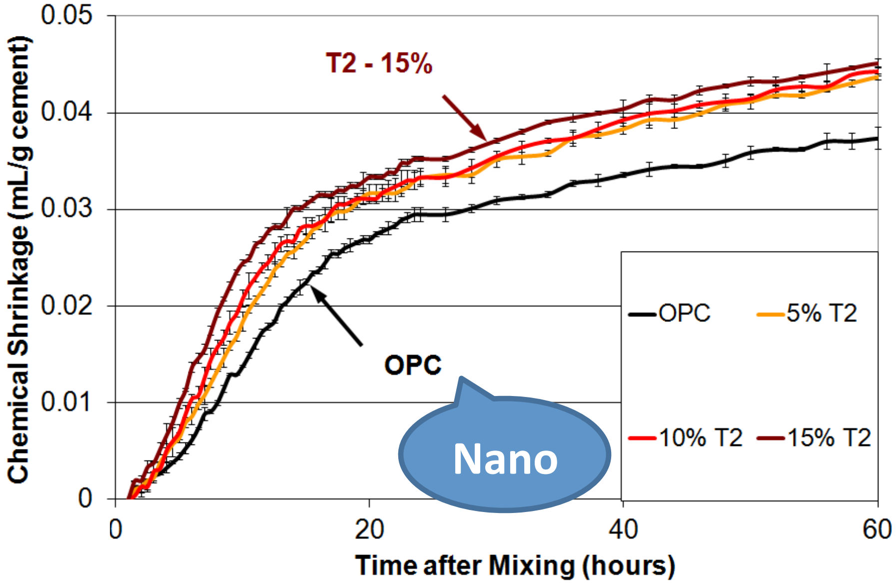
- Compare chemically inert nano- and microparticle fillers in cement-based materials
  - Heat of hydration (isothermal calorimetry)
  - Chemical shrinkage
  - Surface area and pore size analysis
  - Life cycle analysis (LCA)



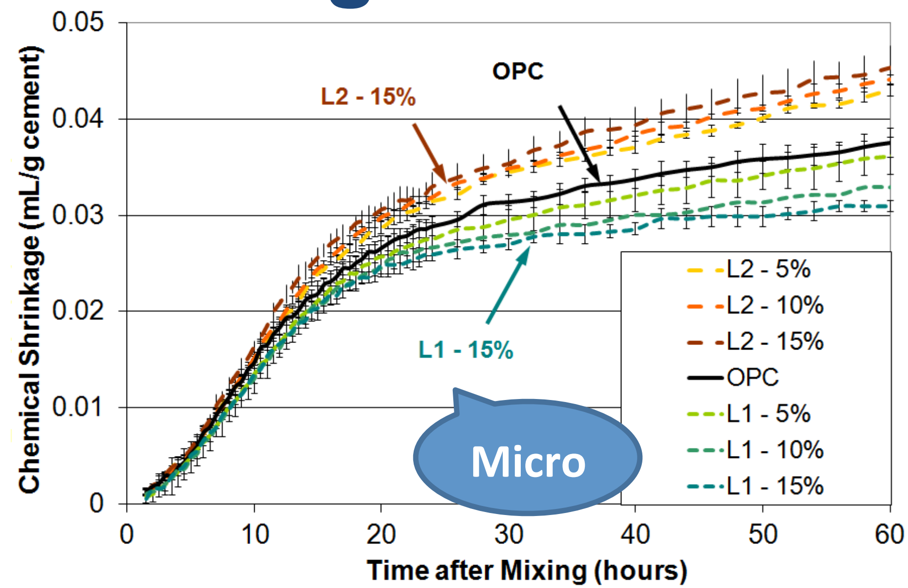




Chemical Shrinkage



Chemical shrinkage of TiO_2-blended cements



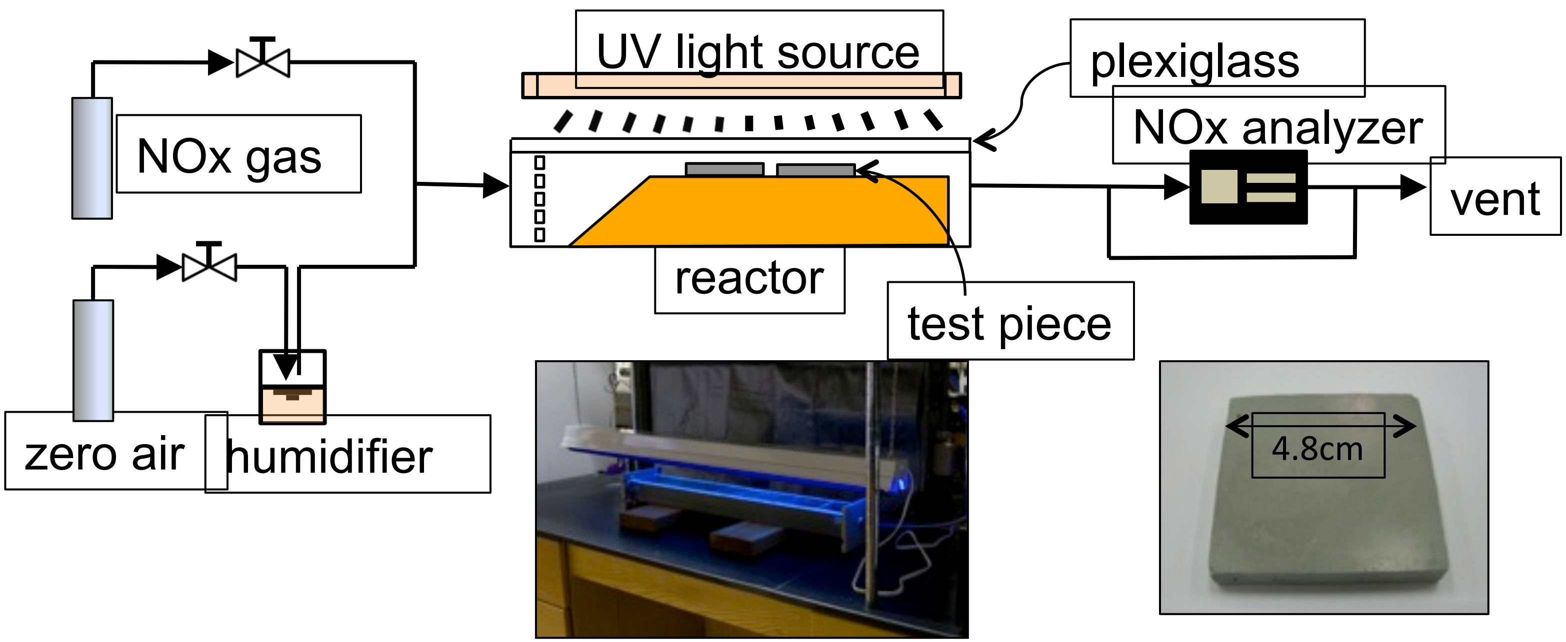
Chemical shrinkage of limestone cements

- Chemical shrinkage: $V_{\text{hydration products}} < V_{\text{water}} + V_{\text{cement}}$
- Related to cumulative heat release, and thus degree of hydration
- Increasing chemical shrinkage with higher nanoparticle (TiO_2) replacement
- Coarser limestone powder (L1) resulted in decreased shrinkage
  - Dilution effect (less cement) dominates over nucleation effect

Microparticles (~20μm) can be used up to 10% with enhanced dimensional stability without compromising degree of hydration.

Photocatalytic efficiency and NOx binding
NO vs. NO_2 (background)

- NO gas is used in most of the photocatalytic tests (ISO and JIS standards) [11-12]. However, the average NO_2/NO ratio on-road was reported to be 0.39 and even higher off-road [13].
- Need to investigate and compare the photocatalytic behavior of cementitious materials under NO_2 as well as NO exposure. *(Photocatalysis Series)*
- NO & NO_2 binding in cementitious materials (without photocatalysis) should also be examined. *(NOx Binding Series)*



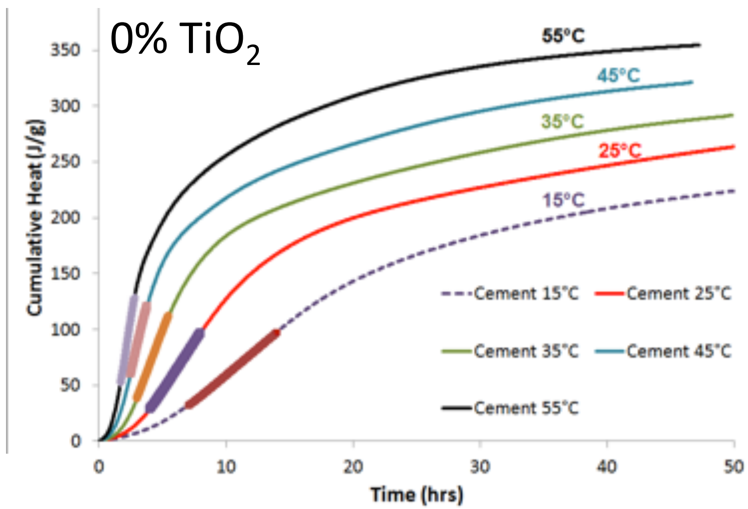
Effect on Hydration: Activation Energy (E_a)

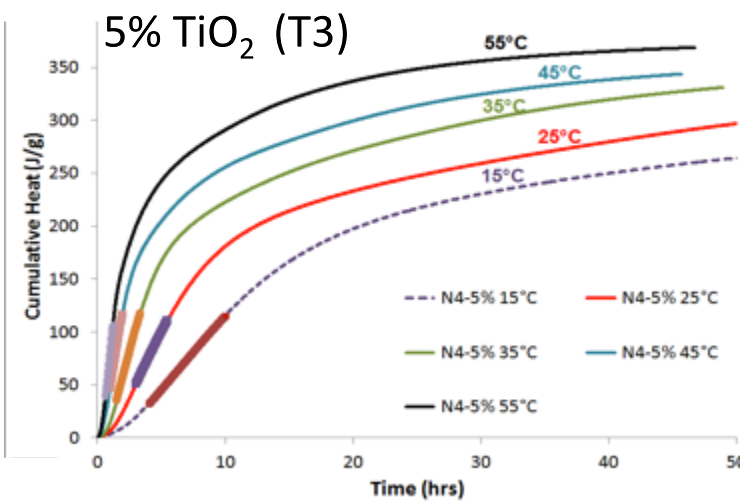
What are the effects of nanoparticles additions to cements?

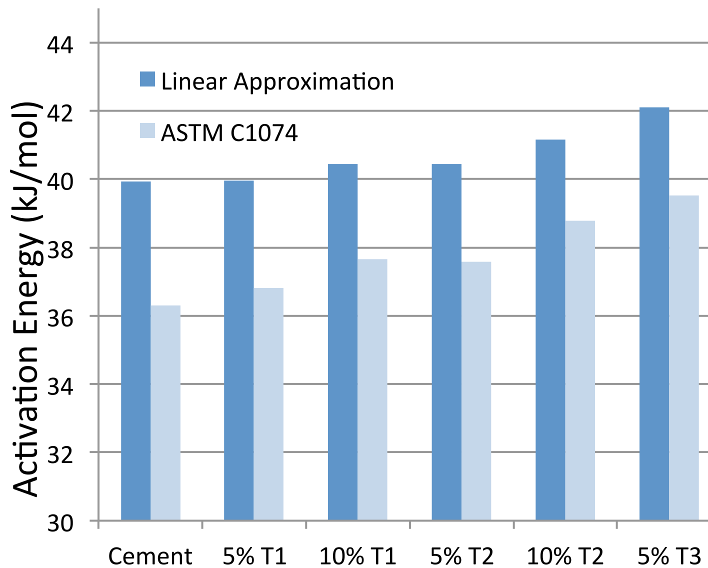
- Temperature sensitivity of cements can be evaluated by estimating the apparent activation energy (E_a)

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

$$E_a = \frac{-\ln\left(\frac{\tau_{ref}}{\tau_c}\right)}{\left(\frac{1}{T_{ref}} - \frac{1}{T_c}\right)} \cdot R$$







- Nano-particles *increase* temperature sensitivity (opposite trend from most SCMs)

Suggests that heterogeneous nucleation on nanoparticles can increase E_a.

Jayapalan, Jue, Kurtis, *J. ACerS*, in review.