# Nanomodification of Cement Based Materials

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**Anna Maria Workshop XIII**

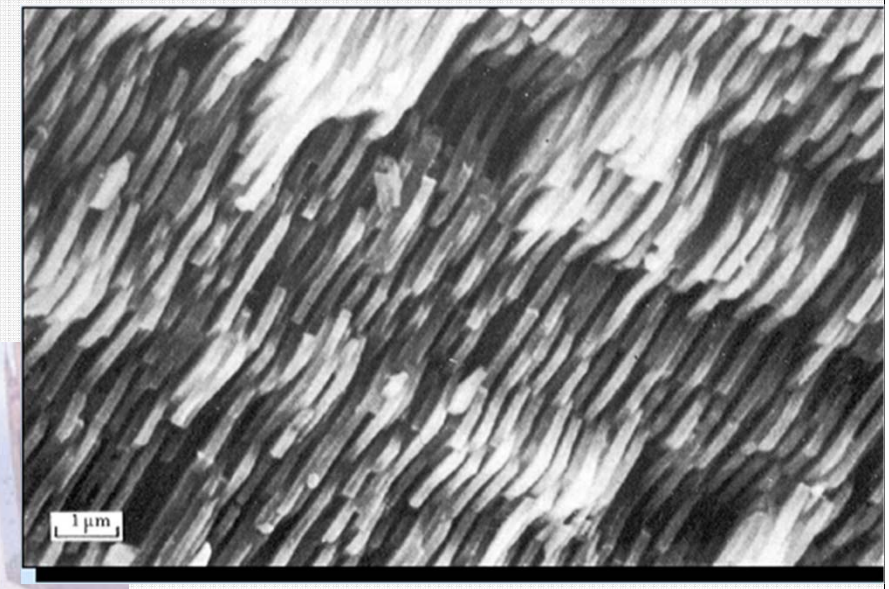
***Unconventional* Concrete, November 7-9**

# Contributing researchers

- Prof. Paramita Mondal, University of Illinois at Urbana-Champaign
- Prof. Raissa Ferron, University of Texas at Austin
- Zoi Metaxa, Northwestern University and Democritus University
- Prof. Maria Konsta-Gdoutos, Democritus University of Thrace
- Dr. Nathan Tregger, Northwestern University
- Dr. Jae Hong Kim, Northwestern University
- Mark Beacraft, Lehigh University
- Dr. John Gaitero, Labein Tecnalia
- Dr. Amedeo Gregori, University of L'Aquila
- Prof. Kejin Wang, Iowa State University
- Jean-Juste Mbele, Schlumberger
- Dr. Thomas Voigt, USG
- Prof. Xiaoyan Liu, Hohai University
- Shiho Kawashima, Northwestern University
- Pengkun Hou, Chongqing University

# An example of nanomodification

Mother of pearl (99% $CaCO_3$) has flexural strength of 100 MPa – an order of magnitude higher than chalk




Structure of mother of pearl

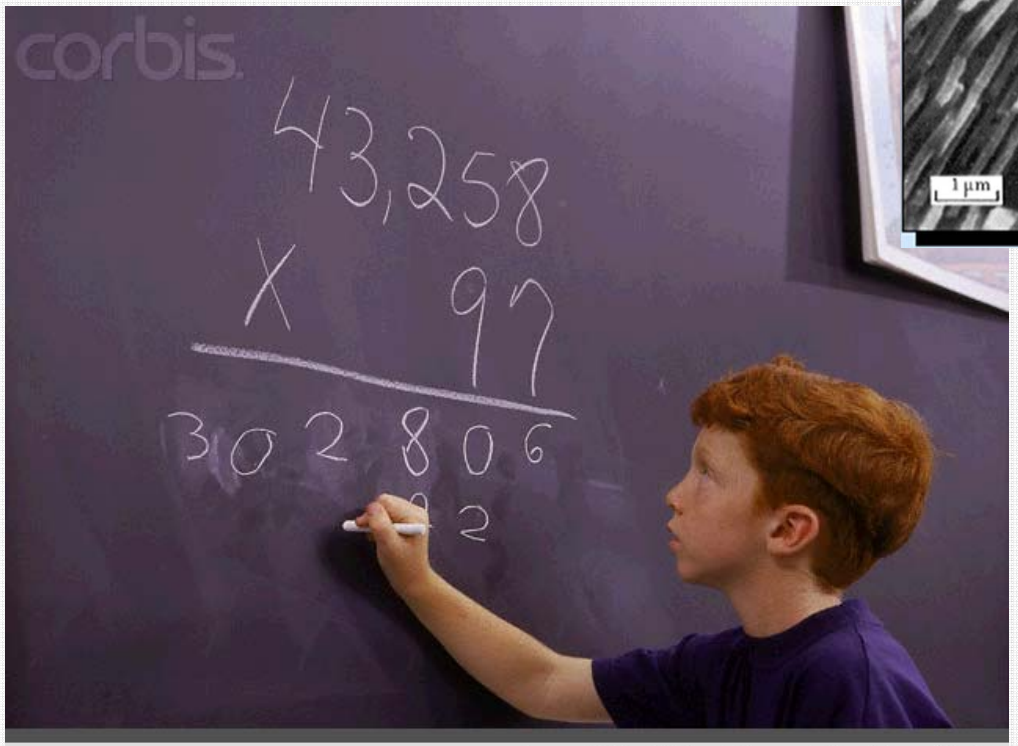



Image: © John T. Wong/Monsoon/Photolibrary/Corbis

# Types of nanoparticles

- ☐ Nanoclay
- ☐ Limestone nanoparticles
- ☐ Nanosilica
- ☐ Titanium dioxide nanoparticles
- ☐ Nanofibers: Carbon nanotubes (CNTs)

Can nanoparticles enhance properties and performance through nanomodification?

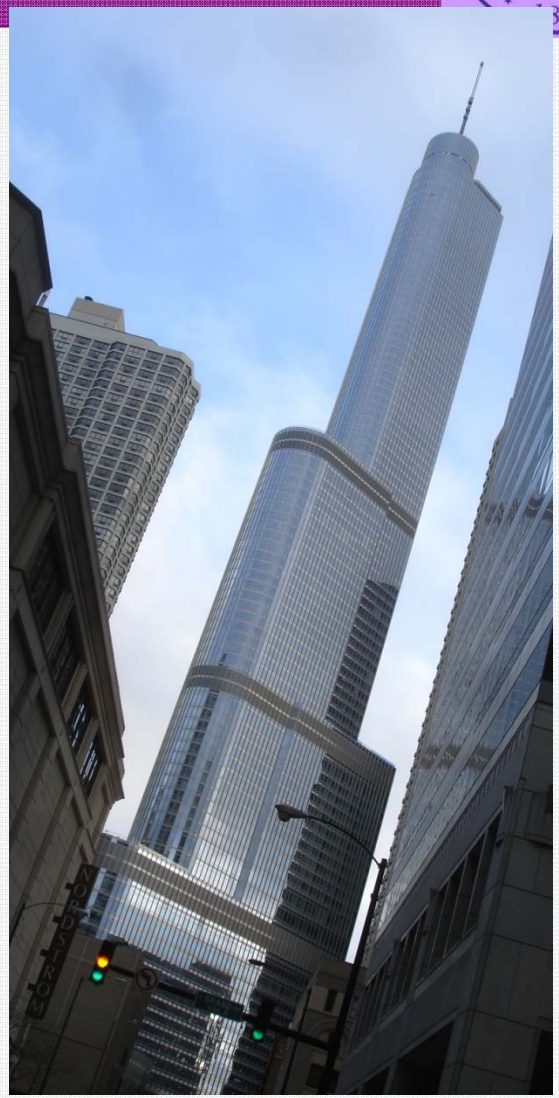
# Outline

- Nanoclays in Flocculation Study
- Nano$CaCO_3$ in HVFA Cement Systems
- Nanosilica
- Photocatalytic Cement-Based Materials
- Carbon Nanotubes as Reinforcement and Sensors

# Self-consolidating concrete (SCC)

Highly flowable concrete that resists segregation and develops its mechanical properties without vibration

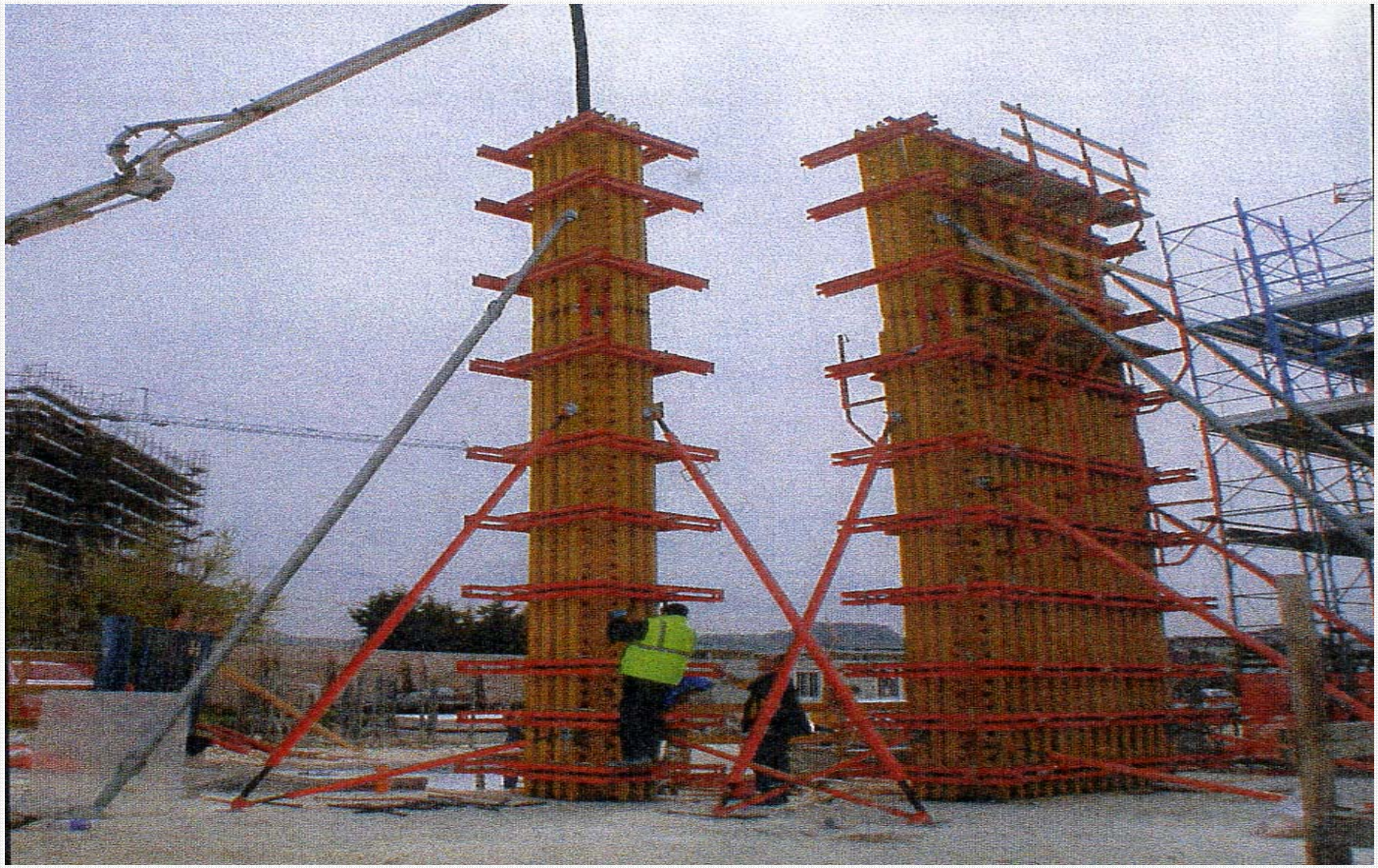
QuickTime™ and a
Cinepak decompressor
are needed to see this picture.



*Trump Tower, Chicago (Courtesy: Tregger)*

→*Take advantage of the high consolidating properties*

# SCC and Formwork Pressure

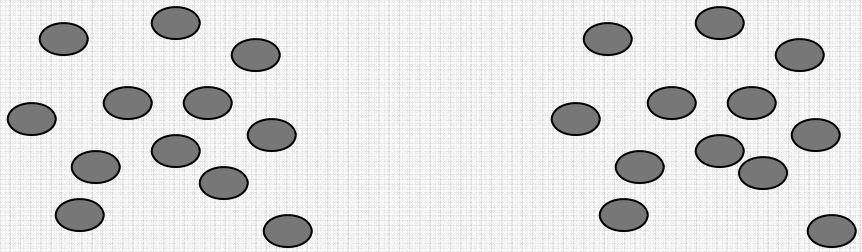


Mock Up Test (2007, Dante Galeota, and et al.)

*Research in collaboration with Université de Sherbrooke and CTL*

# Current Situation

- ACI 347: presumed lateral pressure should equal the hydrostatic pressure until the effect of formwork pressure is understood
- Studies have shown that SCC can have pressure less than hydrostatic[1-3] due to structural rebuilding

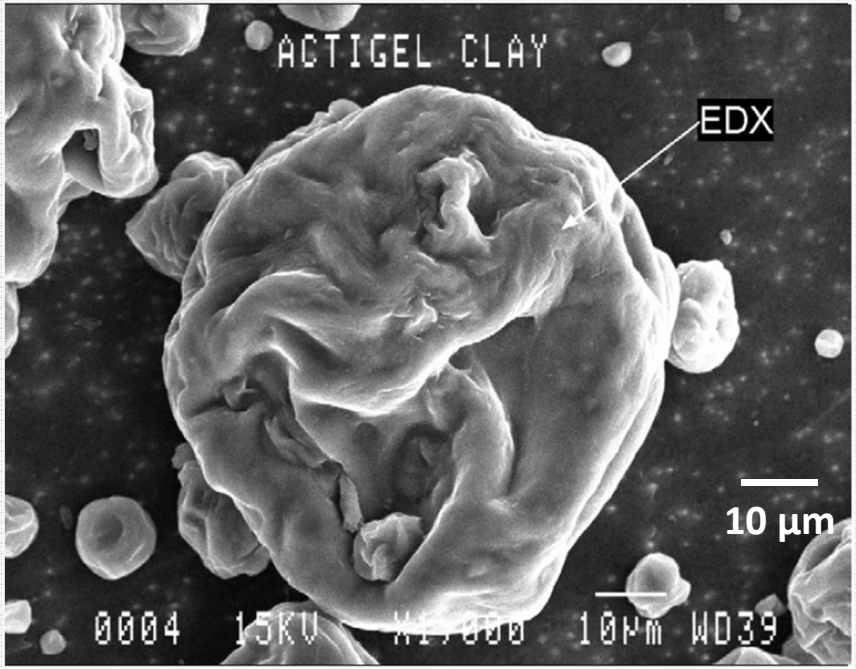


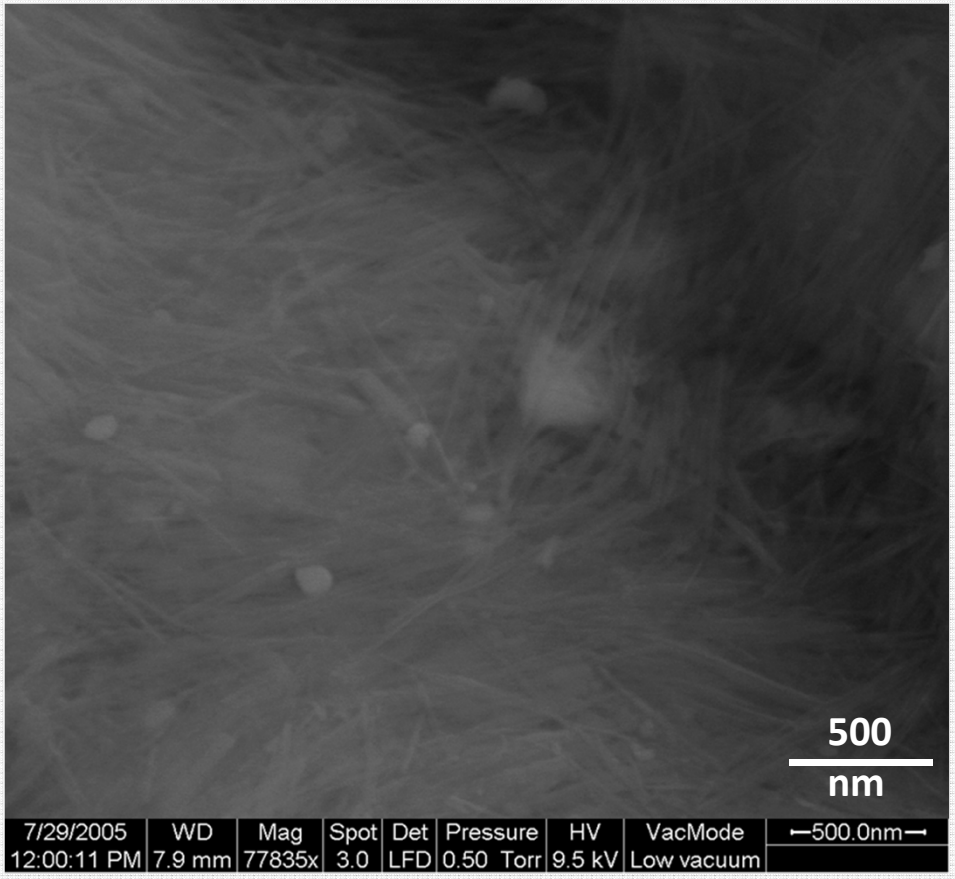

1. A. Assaad, et. al, Cement and Concrete Research, v.35, 2005
2. P. Billberg, et. al, Concrete International, v.27 (10), 2005
3. Y. Vanhove, et.al, *Magazine of Concrete Research,* vol. 56, 2004.

# Effect of dispersion on ActiGel

- During mixing, particles break up into much smaller needle structures

*Mbele*



# Formwork pressure simulation

Simulation Range: Real scale column heights from ~3 m to 20 m, and any casting rates

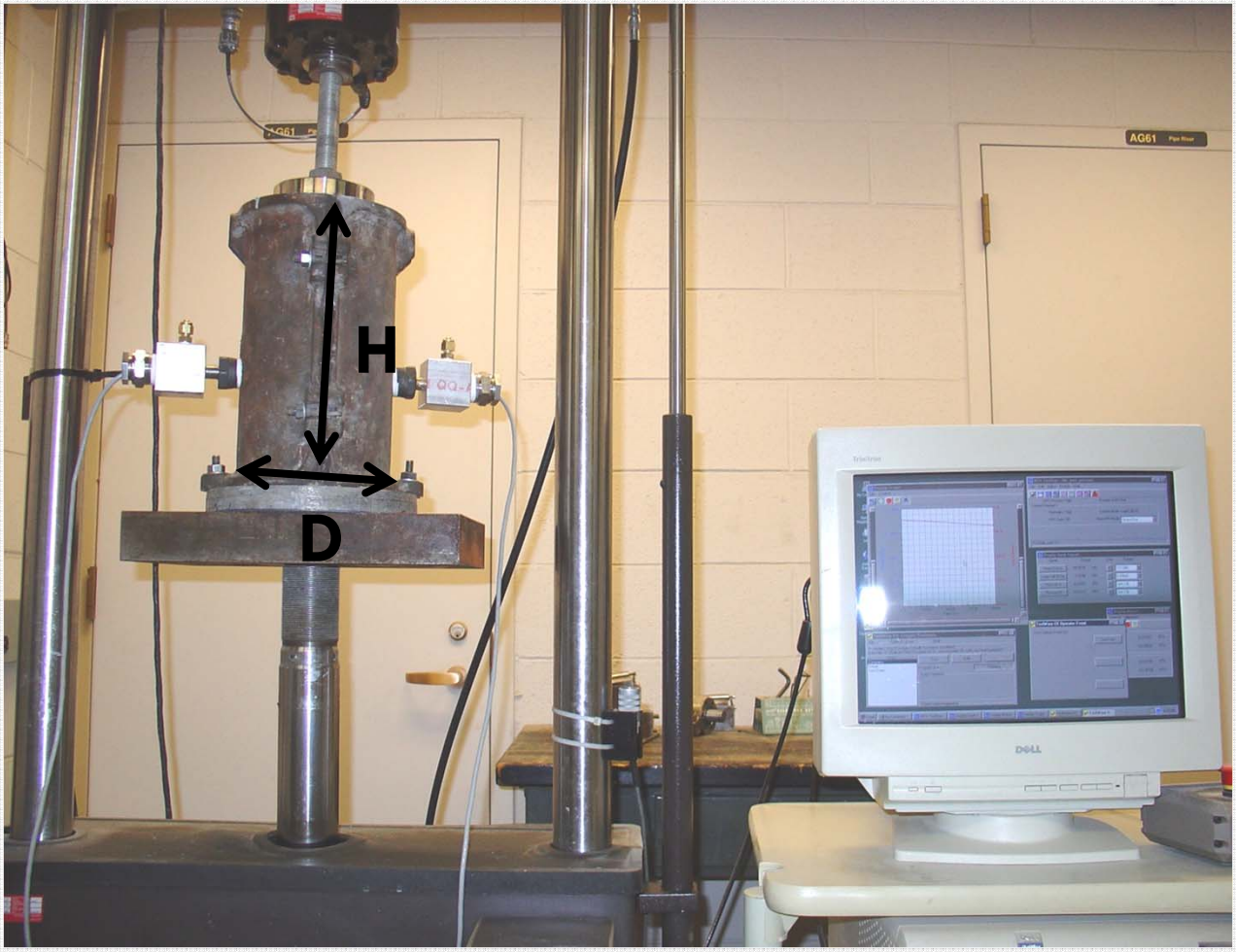
**Pressure Sensors**

(capacity: 50psi = 344kPa)

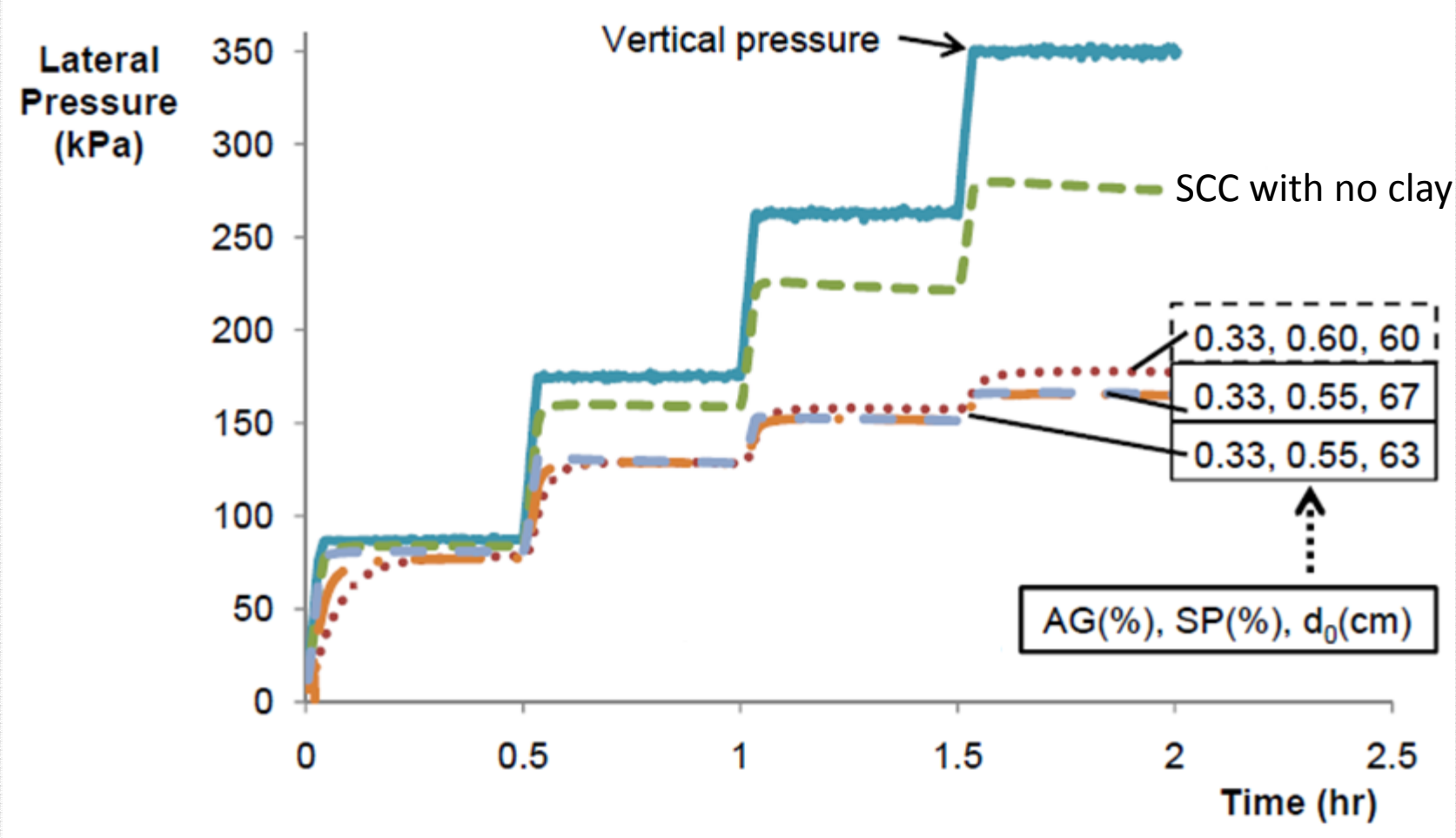
**Lab formwork**

D = 15 cm

H = 30 cm

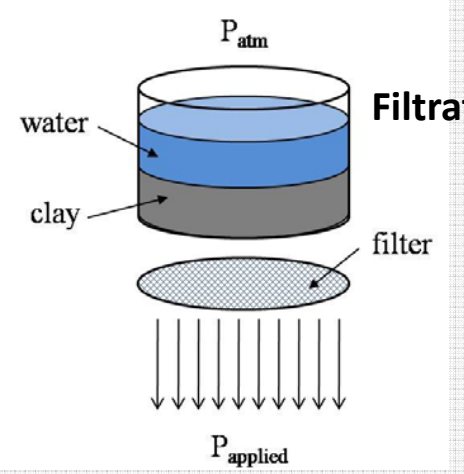


# Clay effect on formwork pressure



# Quantitative measure of clay effect

Methods of investigation:



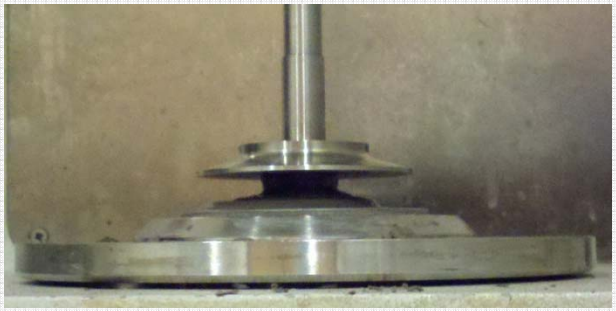

**Filtration test**

**Shear rheology**

**Compressive rheology**


**Floc size determination**

**Tack test**



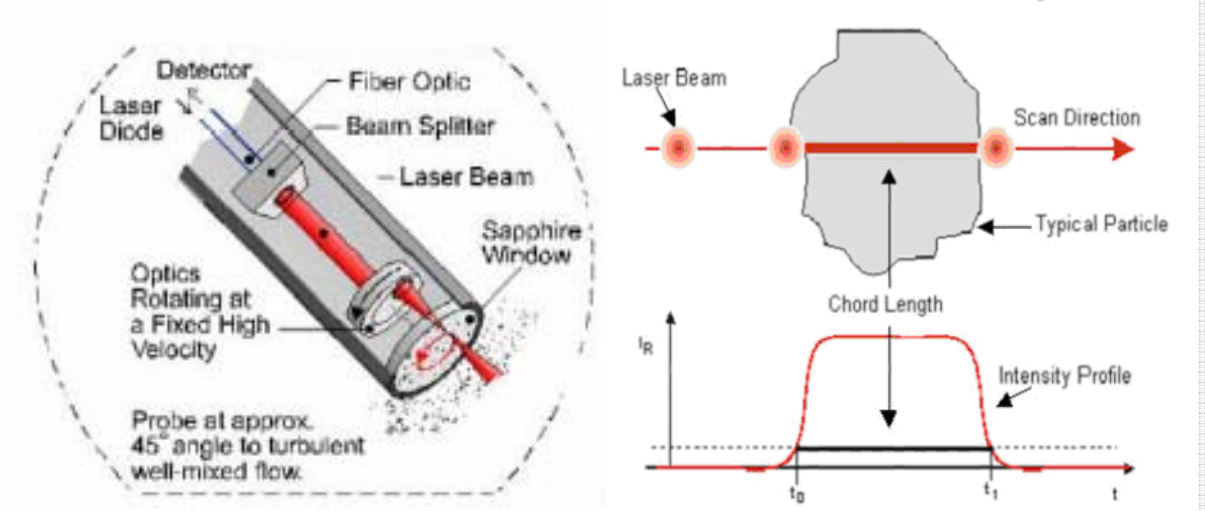
# FBRM: A Way to Measure Floc Size

## Focus Beam Reflectance Measurement (FBRM):

Gives information about Floc size → indirect indication of flocculation

- *in situ/*in-line information about the evolution and size of particle

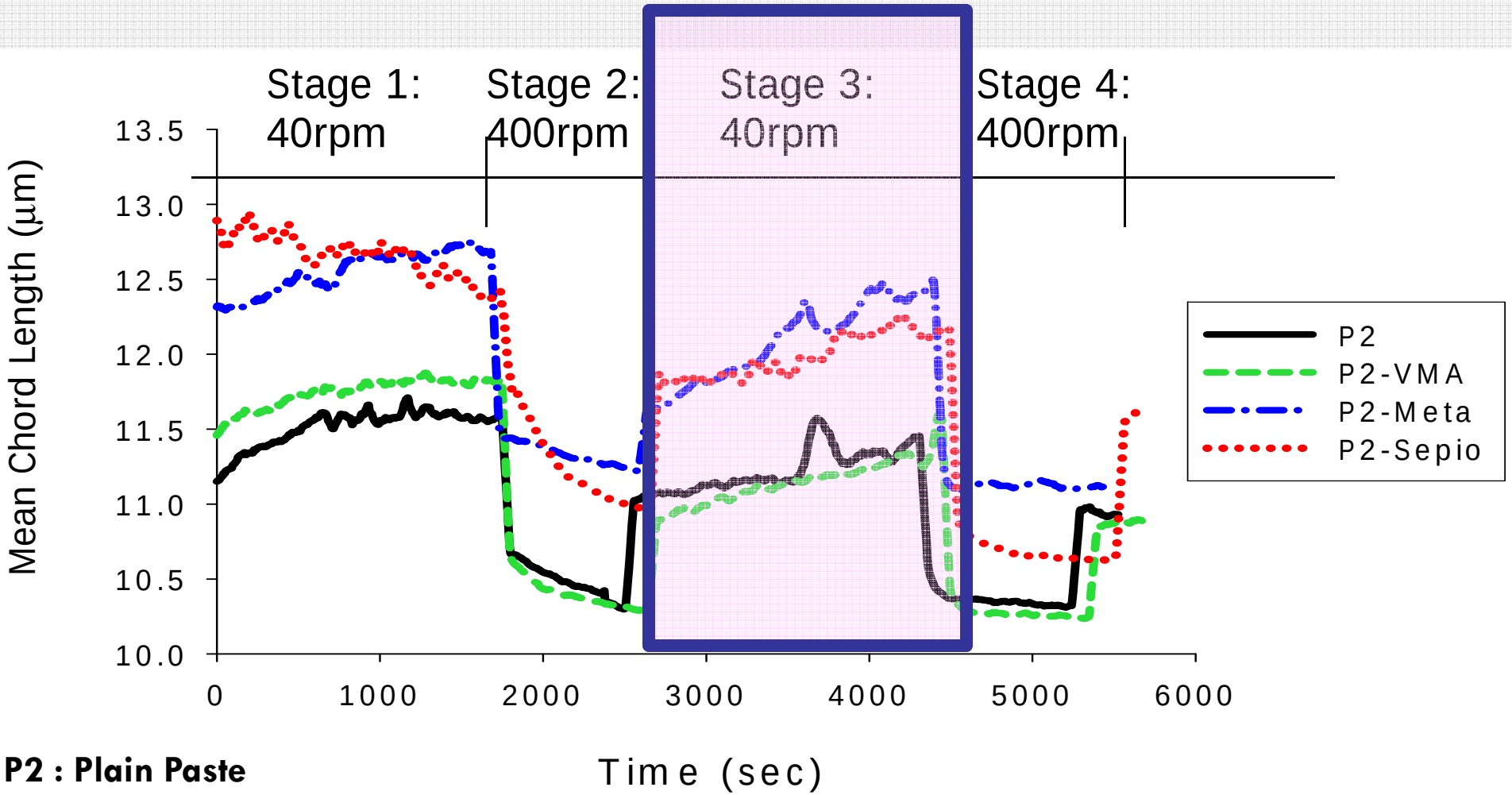
- scans highly focused laser beam across suspension and measure time duration of back scattered light




(Mettler-Toledo, 2005)

- Time taken for beam to scan is measure of particle size
- Focus beam cross particle on a straight line between any 2 points.
- Hundreds of thousands of chords are measured per second
- Chord length range: 0.5 – 1000 µm

# Floc size evolution




**P2 : Plain Paste**

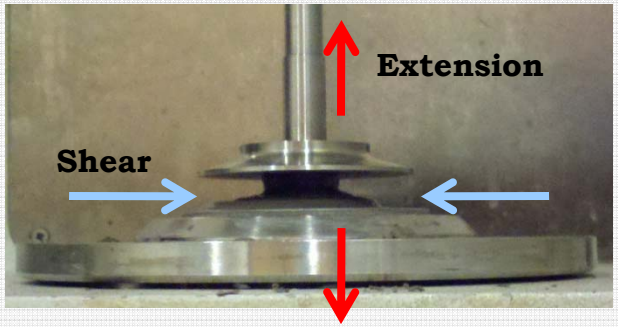
**P2-VMA: Paste with a cellulose-based viscosity-modifying agent**

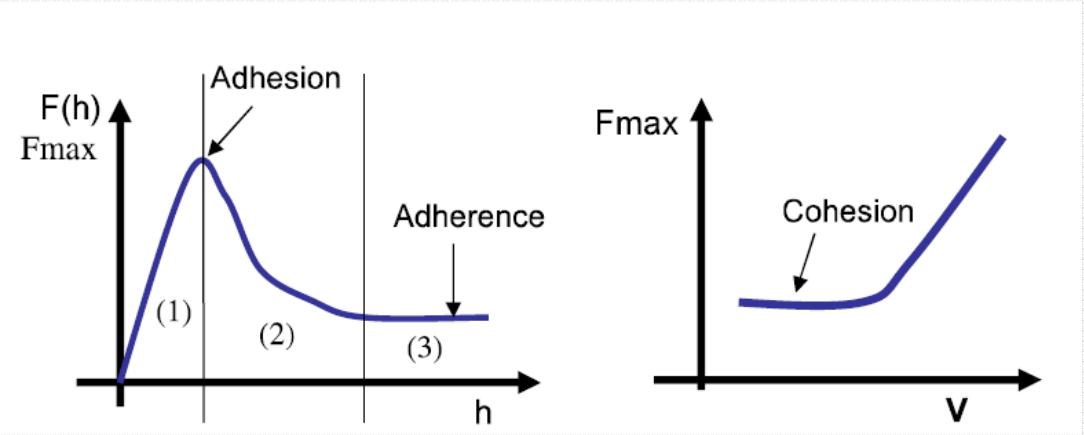
**P2-Meta: Paste with metakaolinite clay (calcined, purified kaolinite)**

**P2-Sepio: Paste mix with sepiolite clay (hydrated magnesium silicate serpentine)**

# Tack test

- Properties measured by tack test include:
  - Adhesion strength
    - Flow resistance and intrinsic cohesion (internal strength) at rest
  - Cohesion strength
    - Static property relating to intermolecular and capillary forces



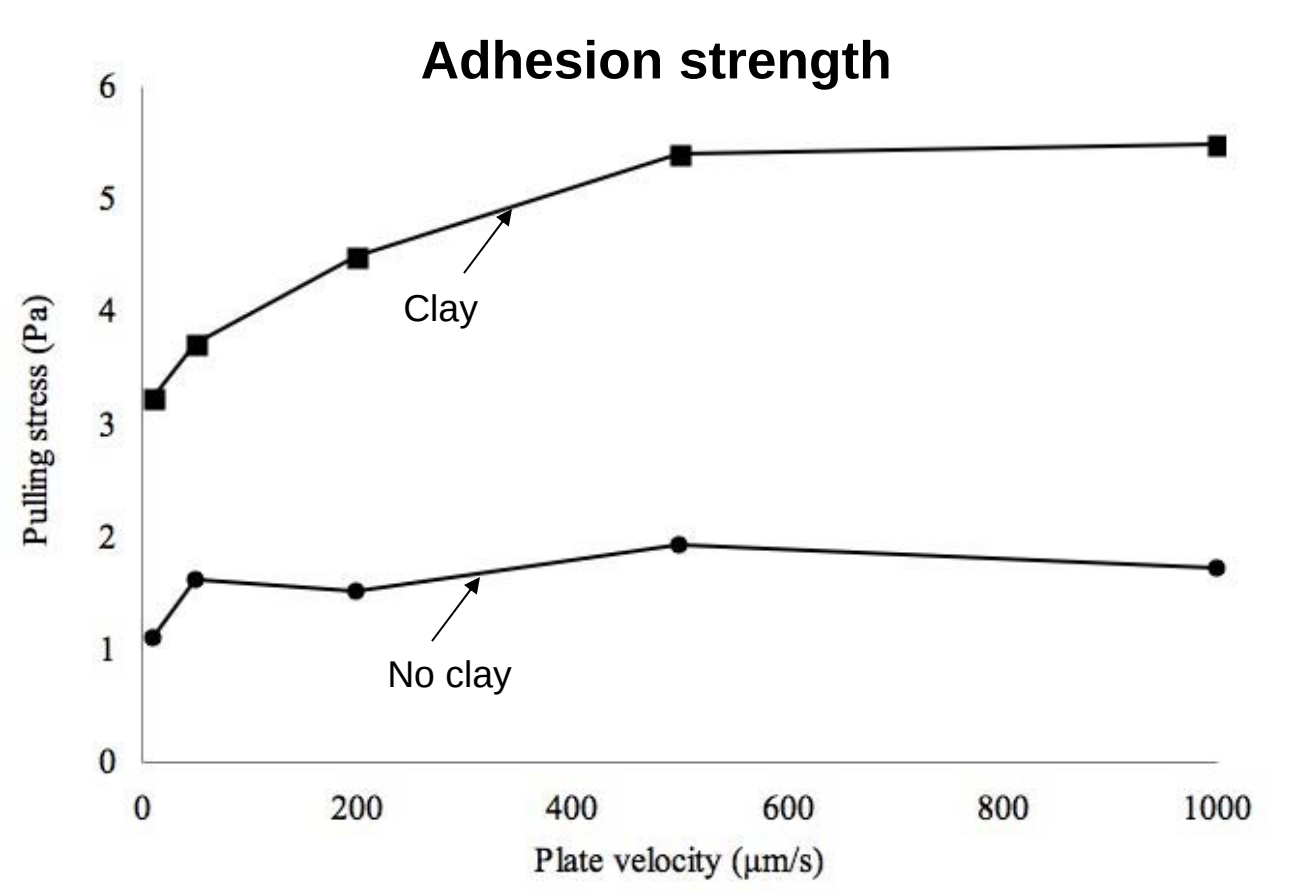




Kaci et al. 2010

# Tack test: Results

Effect of clay:

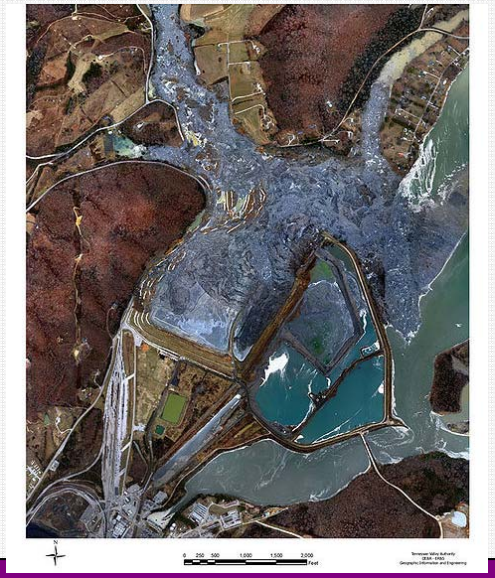
- Cement paste (w/c = 0.43)
- 1% nanoclay



# Outline

- [x] Nanoclays in Flocculation Study
- [ ] Nano$CaCO_3$ in HVFA Cement Systems
- [ ] Nanosilica
- [ ] Photocatalytic Cement-Based Materials
- [ ] Carbon Nanotubes as Reinforcement and Sensors

# Nanoparticles in high-volume fly ash (HVFA) cement systems

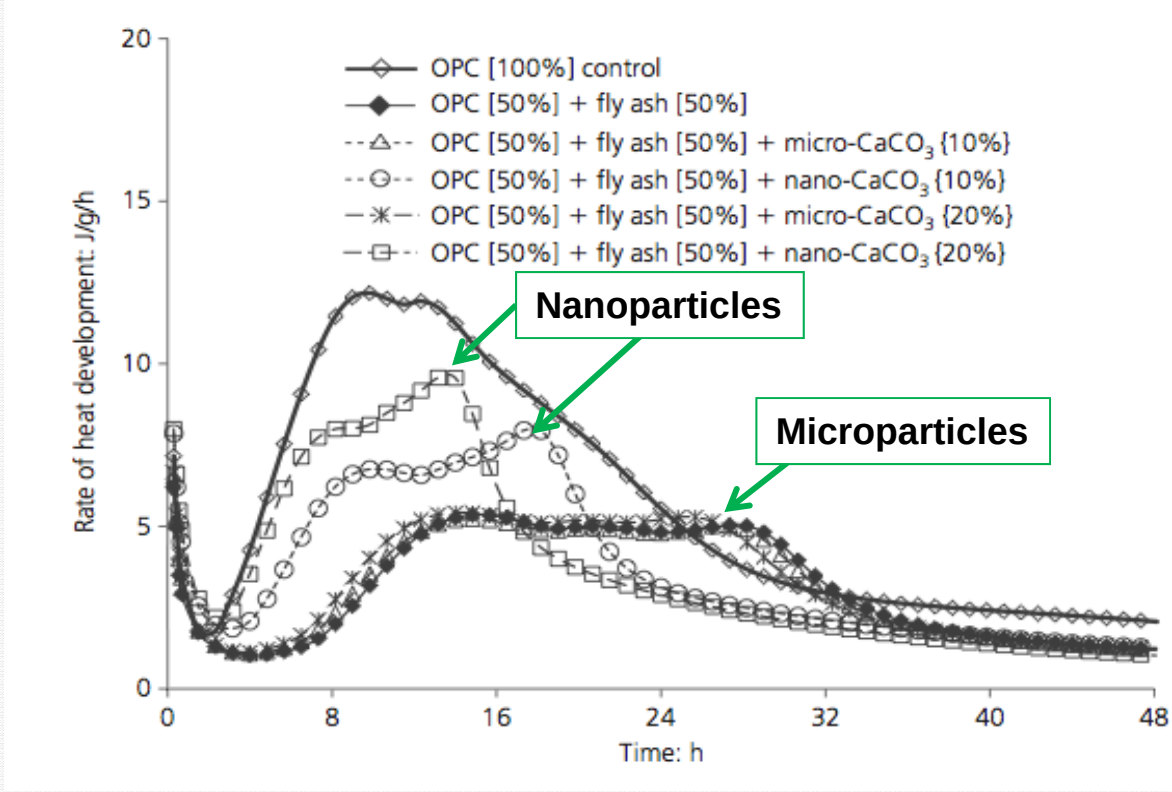


Aerial image of Kingston Ash Slide 12/23/08

- HVFA cementitious materials:
  - Eco-friendly
- Advantages:
  - High flowability
  - Low cement content
  - Low hydration heat
  - Strength gain in the later age
  - Improvement in durability
  - Low costs
- Disadvantages:
  - Low early age strength gain

# NanoCaCO$_3$ on HVFA system

**Rate of hydration**




Sato and Beaudoin 2011

- Effect of size
  - 50% fly ash cement paste
  - **10, 20%** addition of micro- vs nanoparticles

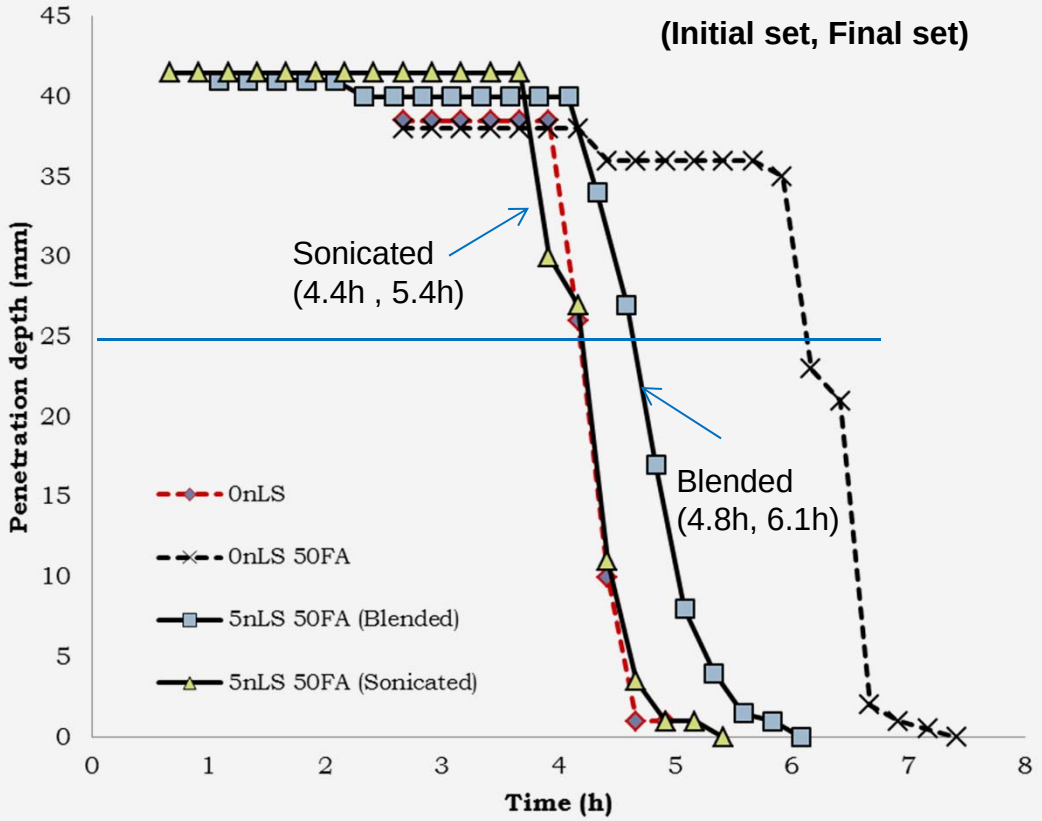
# Ultrasonication


**nanoCaCO$_3$**

**+ water**
**+ superplasticizer**

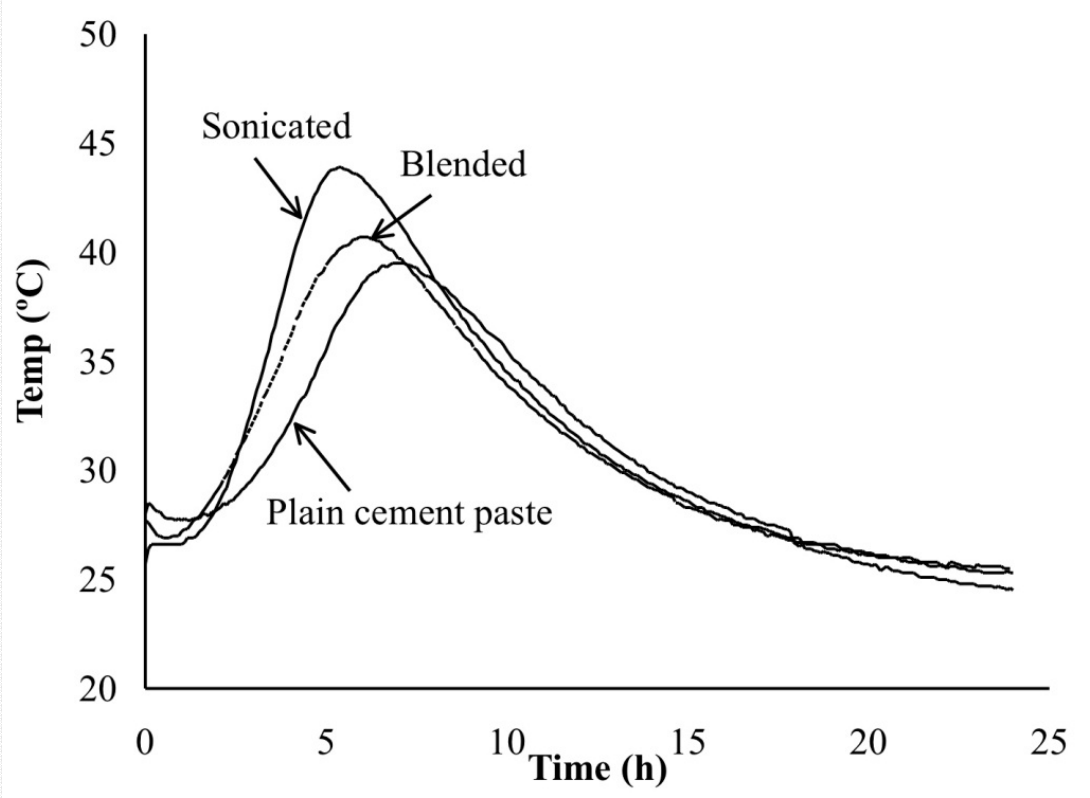
**Sonication (1.5h)**

# Setting time



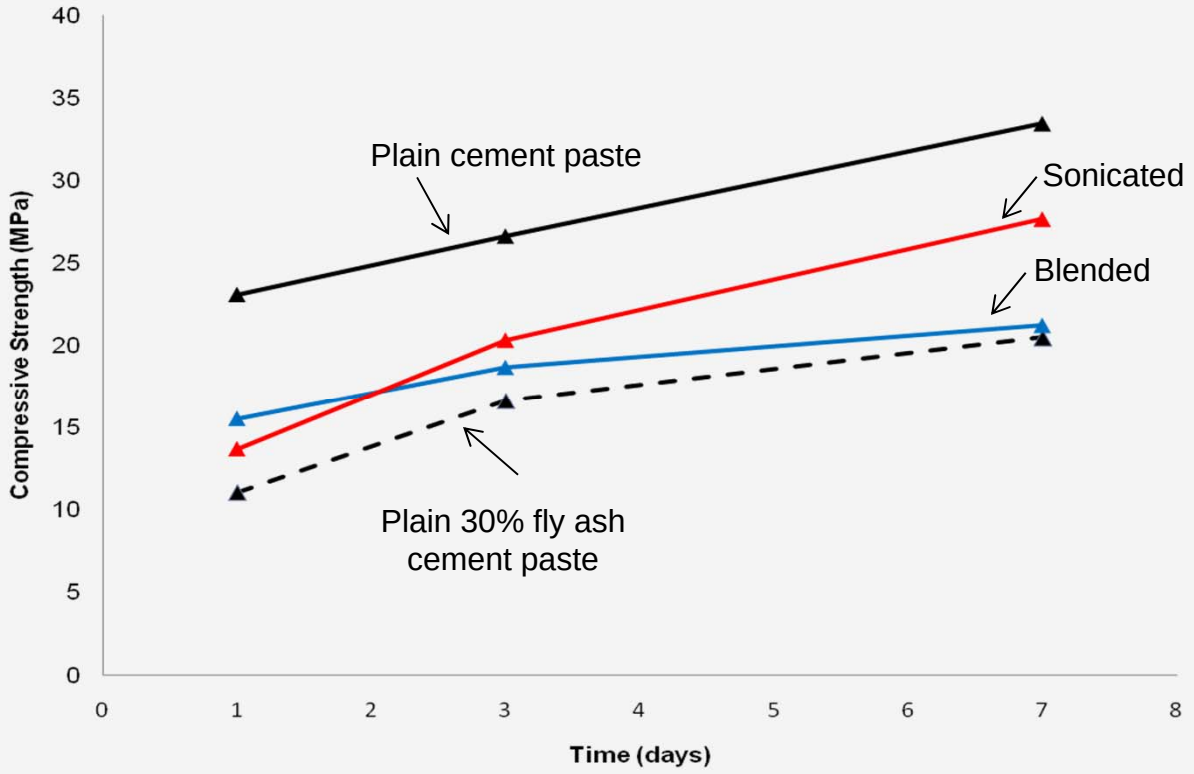

- Effect of dispersion on setting
  - 50% fly ash cement paste
  - **5%** addition of sonicated vs blended nanoparticles

# Rate of hydration




- Effect of dispersion
  - Cement paste (w/c = 0.4)
  - **5%** addition of sonicated vs blended nanoparticles

# Early-age compressive strength gain




- Effect of dispersion
  - 30% fly ash cement paste (w/c = 0.43)
  - **5%** addition of sonicated vs blended nanoparticles

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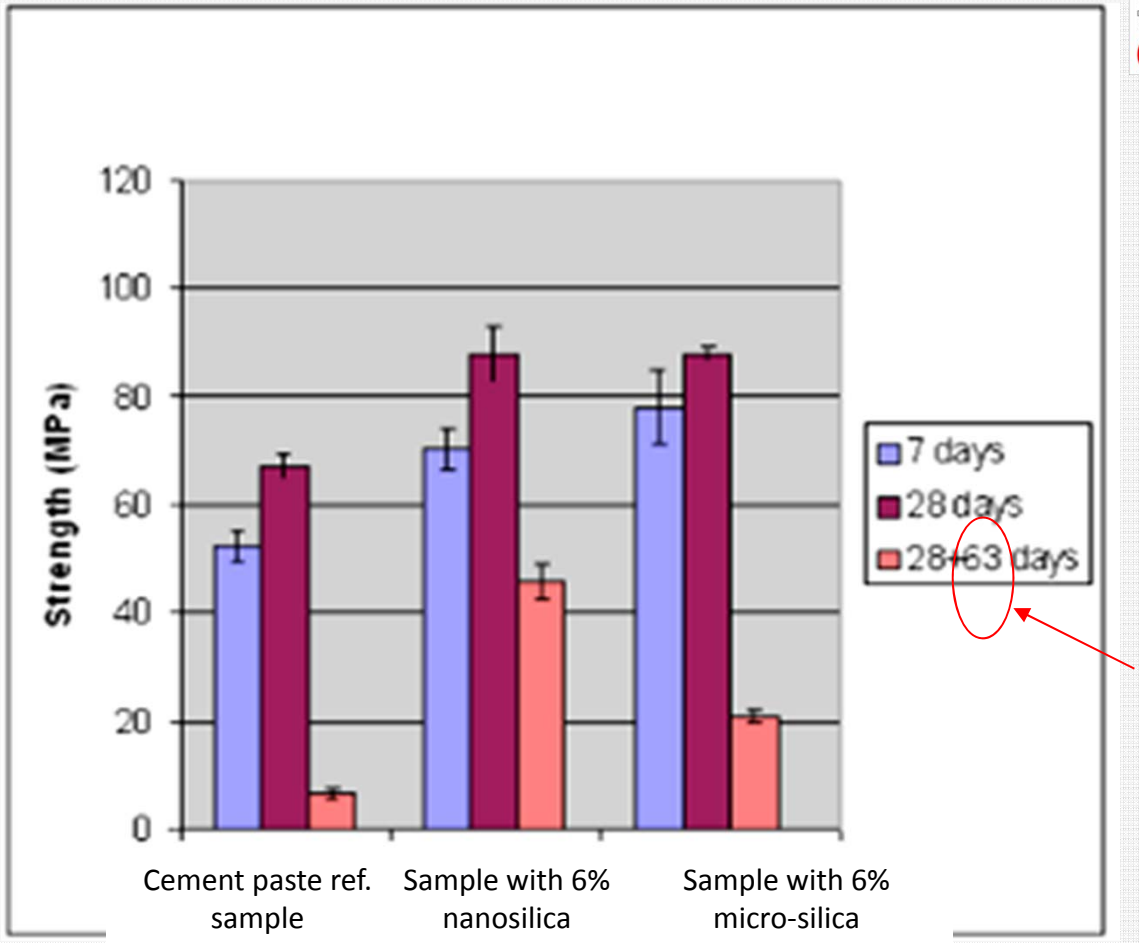
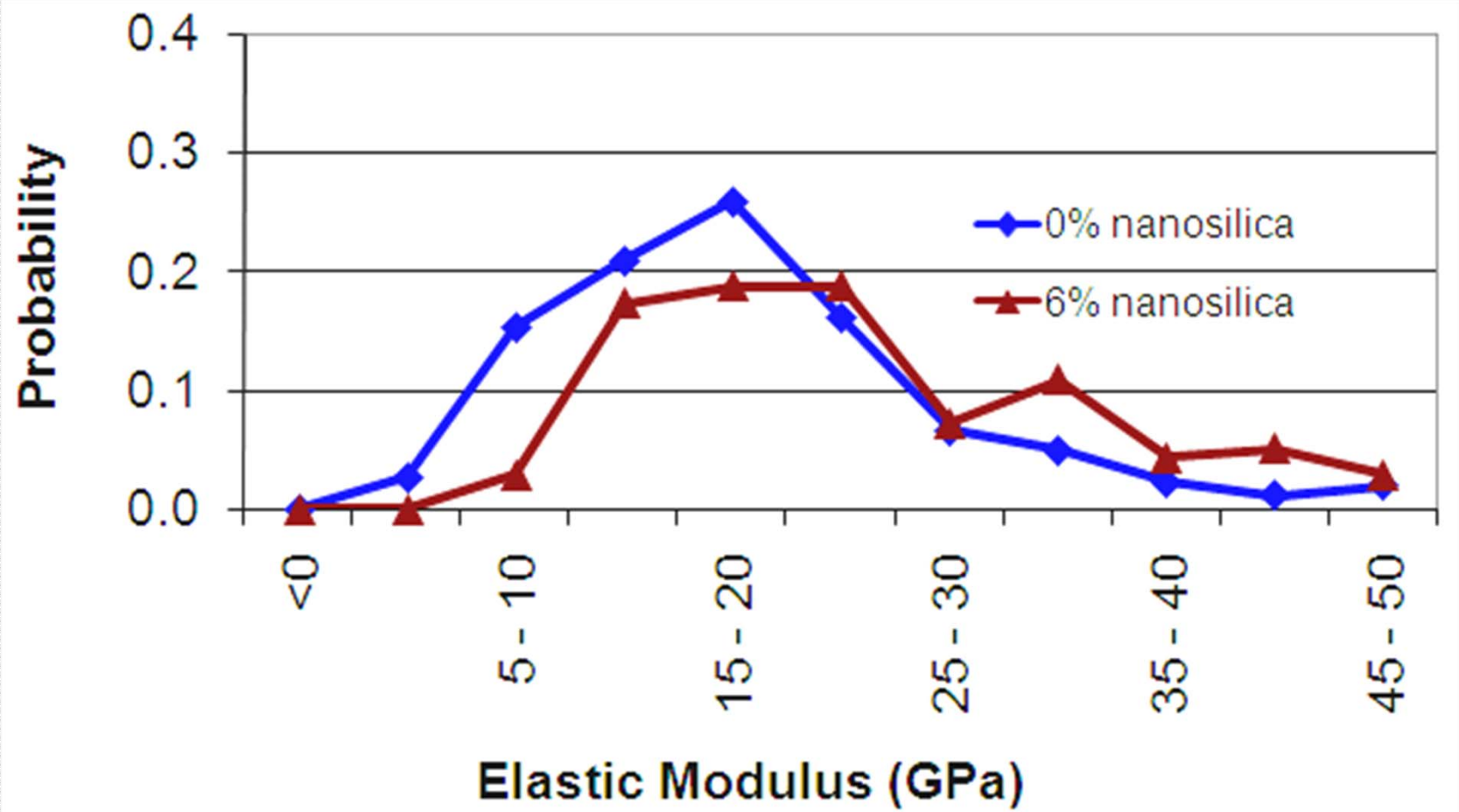
# Results of Compression Test




Degradation

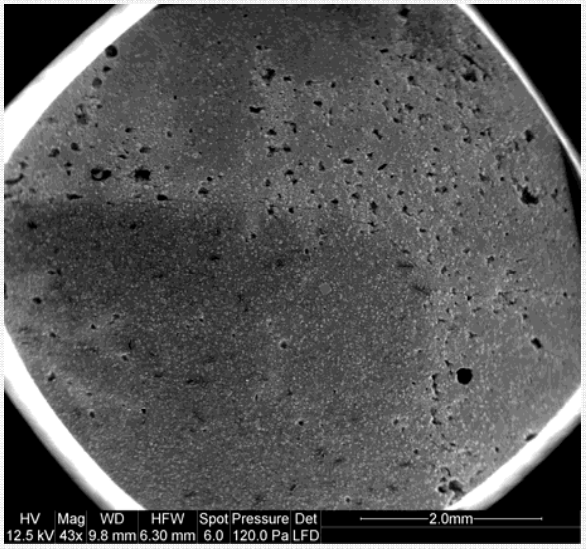
# Nanoindentation Test Results

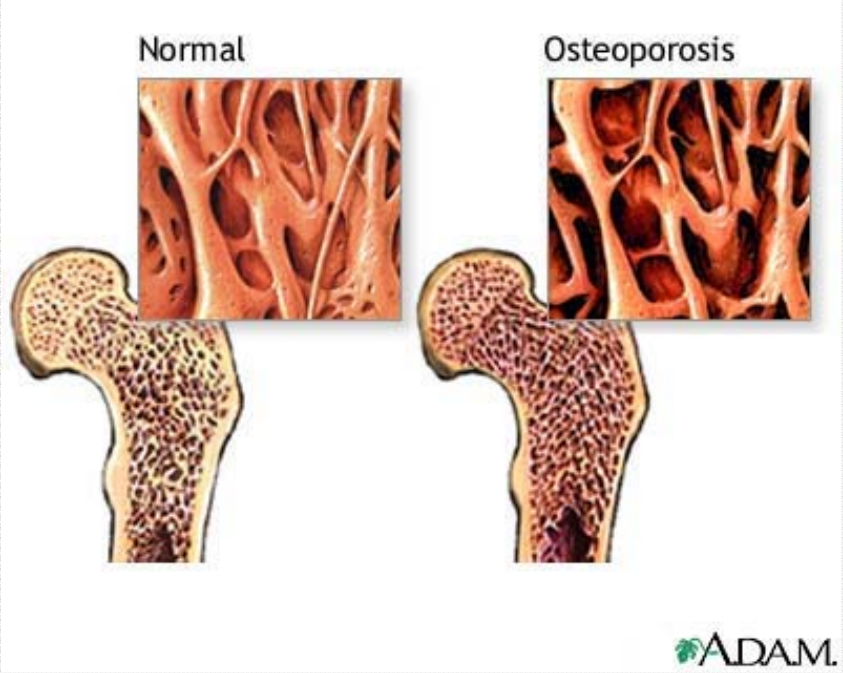
Elastic Modulus of Plain Cement Paste (CP) vs
CP modified with nanosilica



# Calcium Leaching Study of Cement Pastes Modified with Nanosilica

- Nanosilica fill up the gaps in cement paste microstructure and provide denser microstructure
- Reduce the impact of calcium leaching on cement paste.

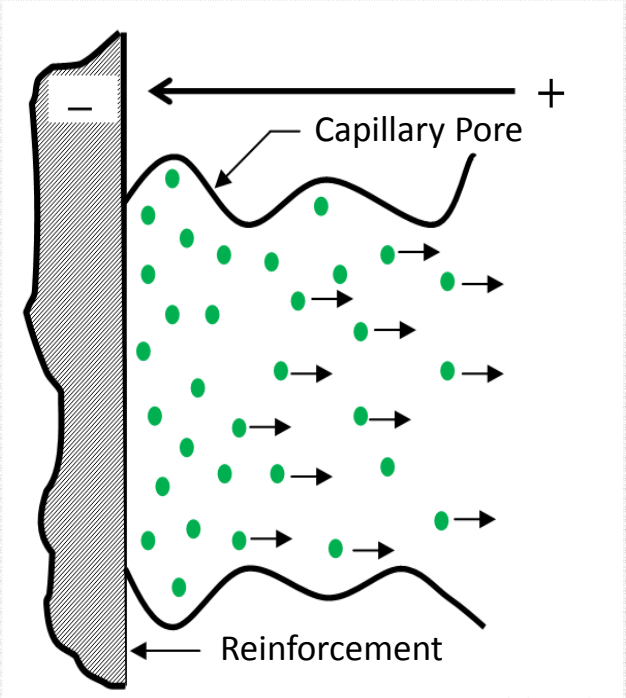


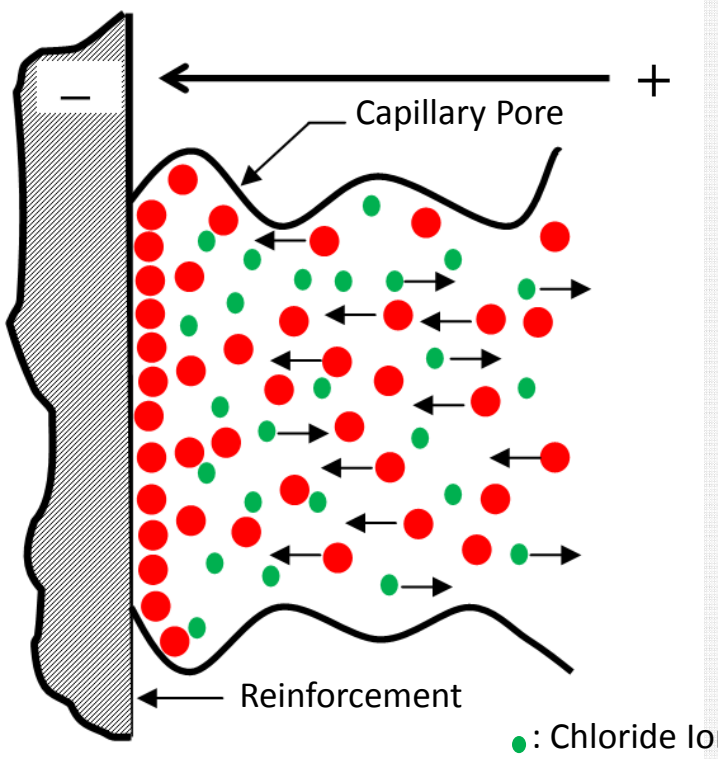

"*Silica Nanoparticle Addition to Control the Calcium-Leaching in Cement-Based Materials,*" J. J. Gaitero*, Y. Sáez de Ibarra, E. Erkizia, and I. Campillo; Physica Status Solidi (a) 203, No. 6, 1313-1318 (2006)

# Electrokinetic Nanoparticle (EN) Treatment to Extend Reinforcement Service Life

## Traditional Electrochemical Chloride Extraction

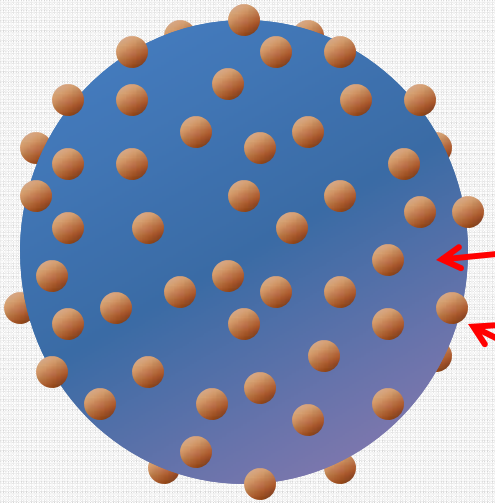



## EN Treatment

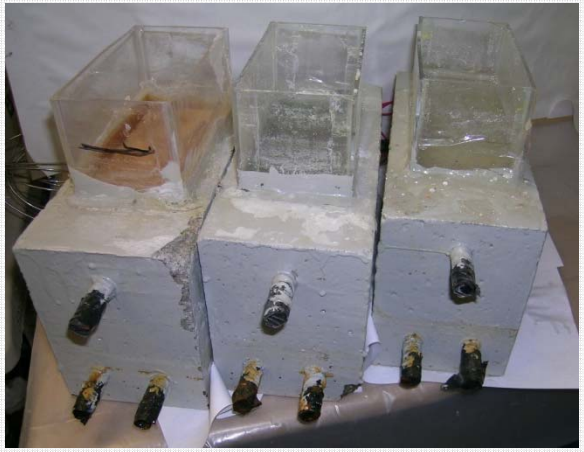



Kupwade Patil. K, Gordon. K, Xu. K, Moral O, Cardenas. H and Lee. L .Corrosion mitigation in concrete beams using electrokinetic nanoparticle treatment,. Excellence in Concrete Construction through Innovation, September 2008, London, UK, pp.365-371.

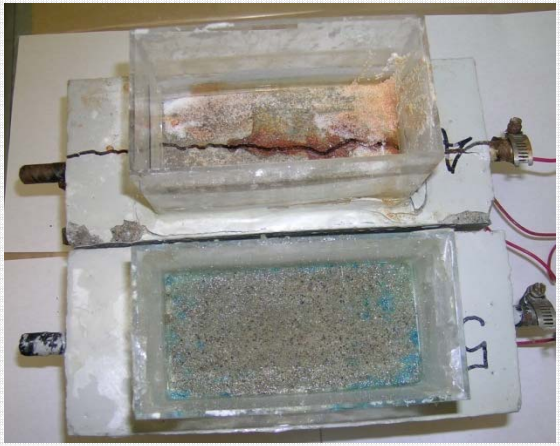
# Pozzolanic Nanoparticle



# ASTM G109 Beams Under Long-term Testing Simulating Bridge Deck Laden with Road Salt



**Bridge Deck Specimens**



**After a year of Salt Testing**

**Unprotected: Severely Cracked**

**Nanoparticle Protected**

Kupwade Patil, K and Cardenas H, .Corrosion mitigation in concrete using electrokinetic injection of reactive composite nanoparticles,.Proc. 53rd International SAMPE symposium, May 2008, Long Beach, CA.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# Photocatalytic cement-based materials

Herald International Tribune

Data 23-11-2006
Pagina 1
Foglio 1 / 2

## Italians discover a smog-eating cement

By Elisabetta Povoledo

**VENICE:** When the American architect Richard Meier was asked to create a church in Rome to commemorate the 2,000th anniversary of Christianity, he designed an imposing white concrete structure dominated by three soaring "sails."

The project's main technical sponsor got to work on a cement that would enhance Meier's trademark white sculptural forms. It came up with a material that essentially cleans itself, minimizing the need for maintenance.

What the sponsor, Italcementi Group, did not know at the time was that the new material — which contained titanium dioxide, a compound used as a white pigment — had another peculiarity. It "eats" surrounding smog.

Extensive testing, sponsored in part by a European Union research project into "smart" antipollution materials, has since determined that construction products containing titanium dioxide help to destroy air pollutants found in car exhaust and heating emissions, scientists say.

Several companies are now developing "smog-eating" products that can be used not just for the facades of buildings, but also in paint, plaster, and paving materials for roads. The new environment-friendly substances are quietly being tried out in buildings, squares and highways in Europe as well as Japan.

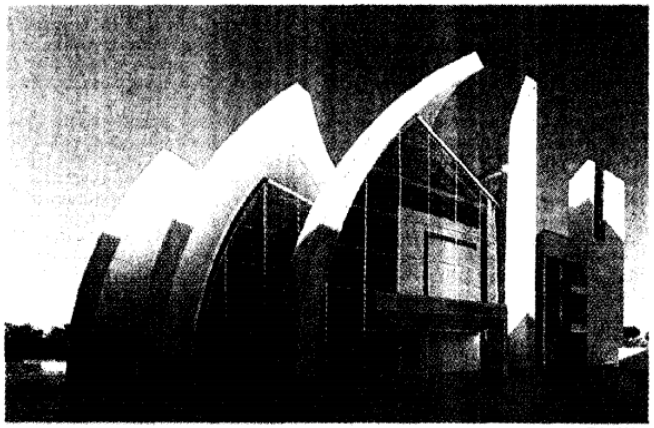
Hailed by some scientists as a breakthrough, the process is still being evaluated by others. The question, said Melanie Sattler, professor of civil and environmental engineering at the University of Texas in Arlington, is "whether coatings on buildings would be able to treat enough of the atmospheric air to make a difference."

Italcementi began developing its product after Meier got his assignment to build the Dives in Misericordia church in 1996 and asked for help.

Titanium dioxide had been used in self-cleaning coatings before because of its photocatalytic properties: sunlight touching the compound triggers a chemical reaction that accelerates natural oxidation.

Upon testing its new cement,

SMOG, Continued on Page 4



Taipei Liao

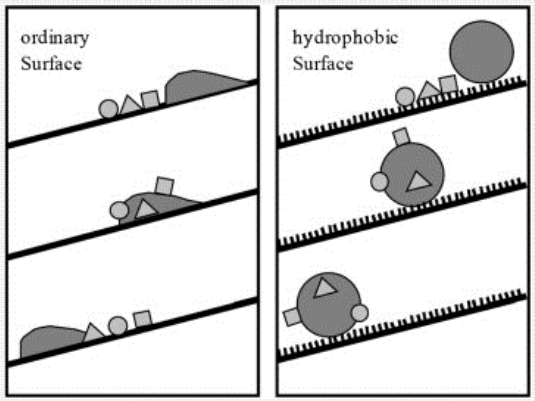
A new material used in the Dives in Misericordia church in Rome, designed by the U.S. architect Richard Meier, contains a compound that "eats" surrounding smog.

http://www.concretedecor.net

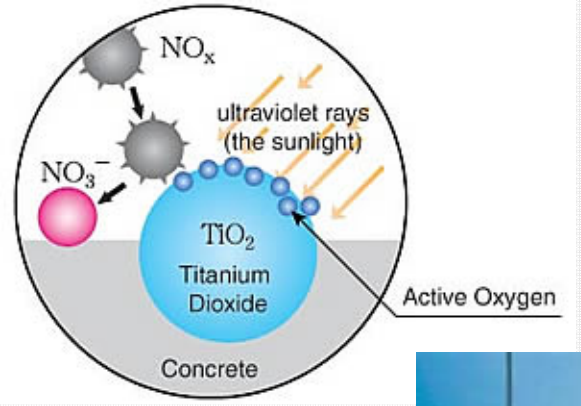
http://www.italcementigroup.com/NR/rdonlyres/A8A7F53C-BA0E-4429-A07C-8C22D45DC18D/0/Herald_Tribune_231106.pdf

# Photocatalytic cement-based materials

## Self-cleaning (Lotus effect)



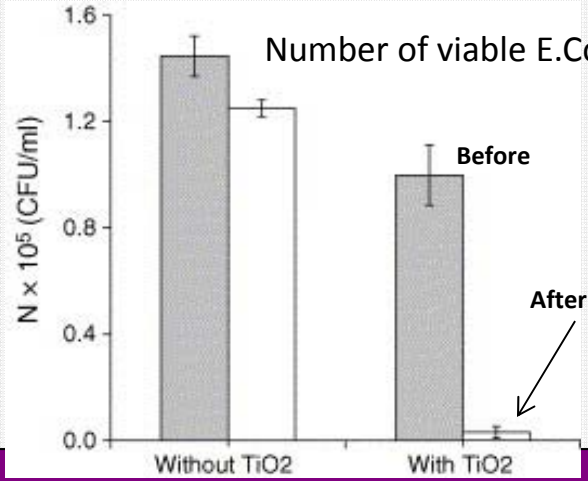

## Air-cleaning




http://www.concretedecor.net

Photocatalytic concrete unit pavers (Japan)

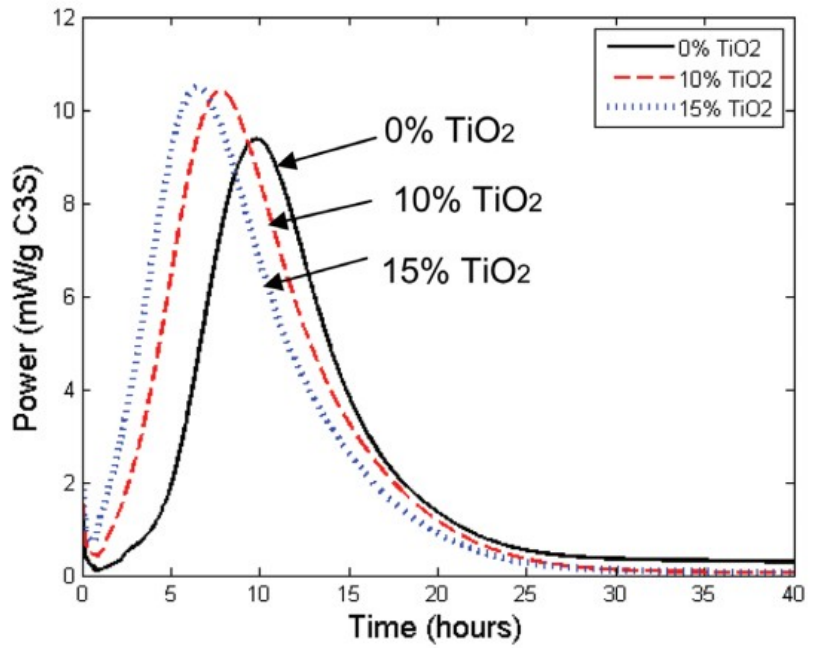
## Self-disinfecting



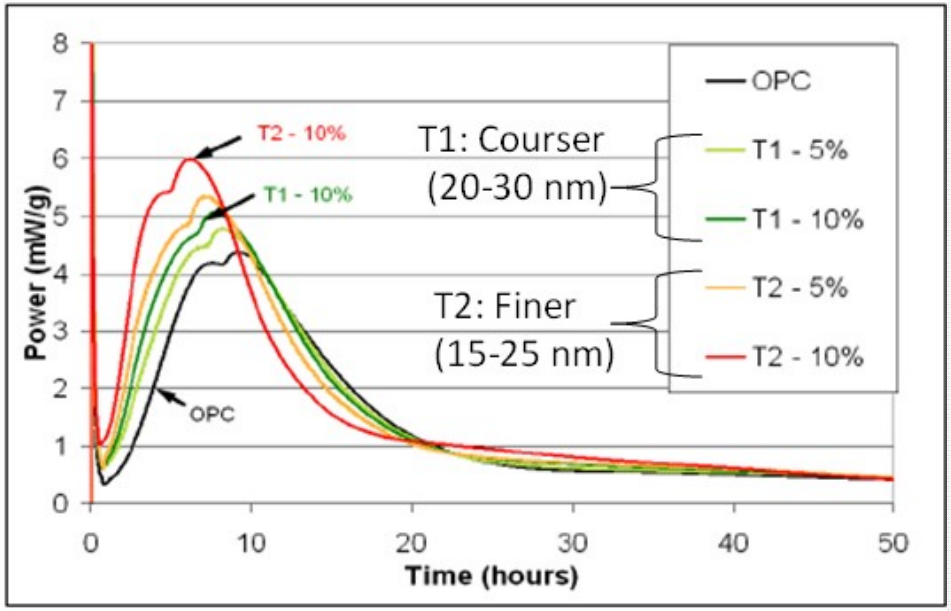

Dadjour et al. 2005

# $TiO_2$ nanoparticles

Rate of hydration reaction of ordinary Portland cement and $TiO_2$ blended cements




Lee et al., 2009



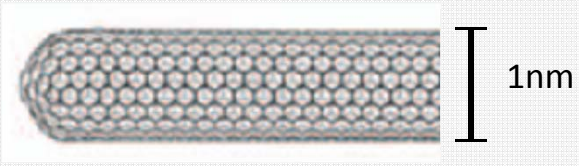

Jayapalan et al., 2009

# Outline

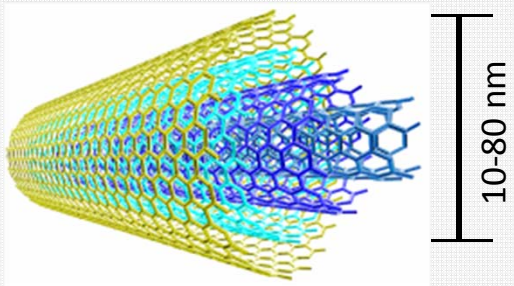
- ☑ Nanoclays in Flocculation Study
- ☑ NanoCaCO$_3$ in HVFA Cement Systems
- ☑ Nanomechanical Properties for Construction Materials
- ☑ Electrokinetic Nanoparticle (EN) Treatment for Corrosion Mitigation
- ☑ Photocatalytic Cement-Based Materials
- ☐ Carbon Nanotubes as Reinforcement and Sensors

# Carbon Nanotubes (CNTs)

- A CNT is a sheet of graphite rolled up into a tube structure and can be described as:
  - Single walled (SWNT)
    - A single sheet has been rolled up with diameter close to 1nm
  - Multi walled (MWNT)
    - A number of sheets have been rolled up with diameter ranges from 10-80nm



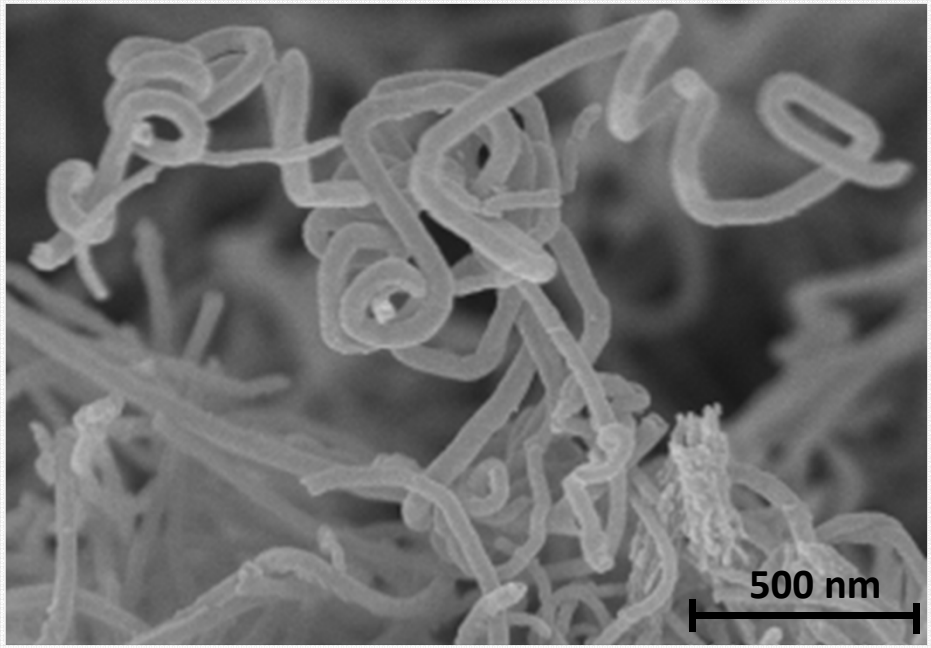

*SWCNT*

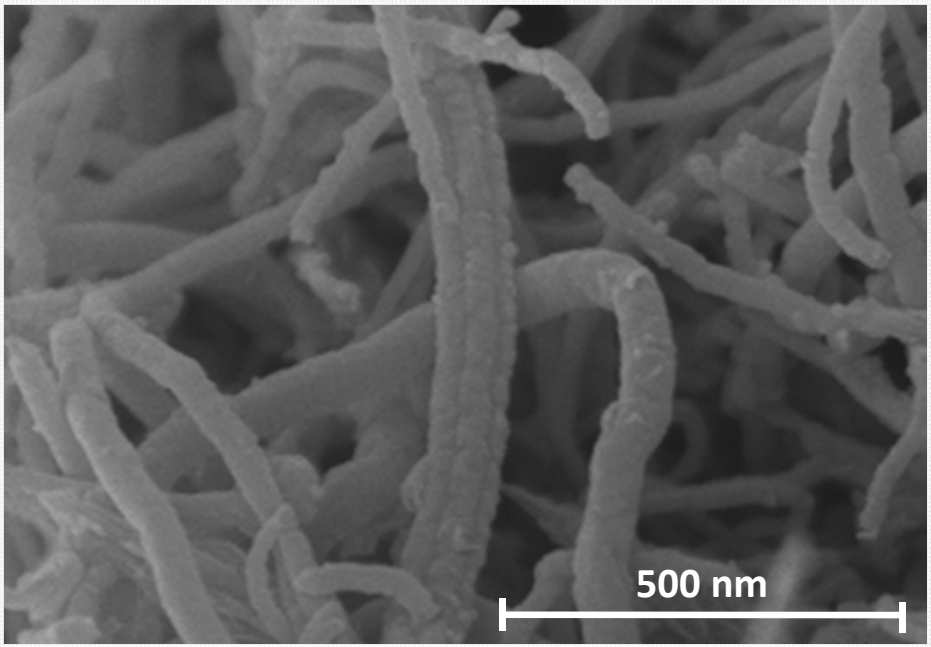



*MWCNT*

# CNTs Dispersion-Main Challenge

- CNTs tent to adhere together due to Van der Waal forces




*SEM images of poorly dispersed CNTs forming bundles in 18h cement paste*

# ACBM Dispersion Method

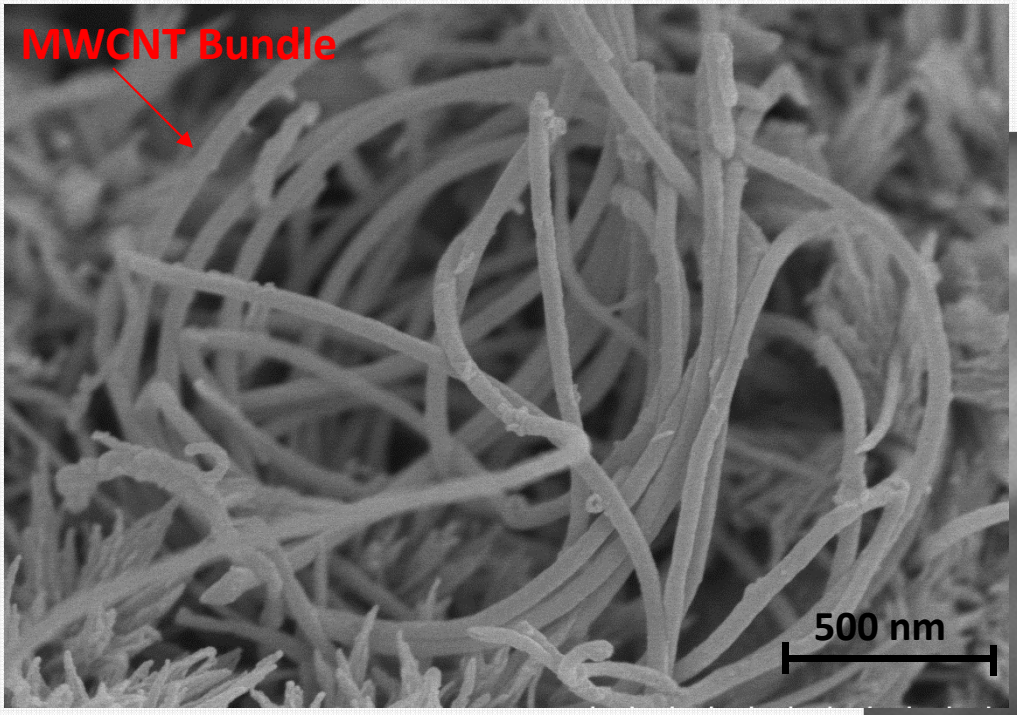
**Goal – <u>Effective Dispersion of MWCNTs in Aqueous Surfactant Solution</u>:**

- Ultrasonic energy by sonication
- Surface treatment with commercially available surfactant

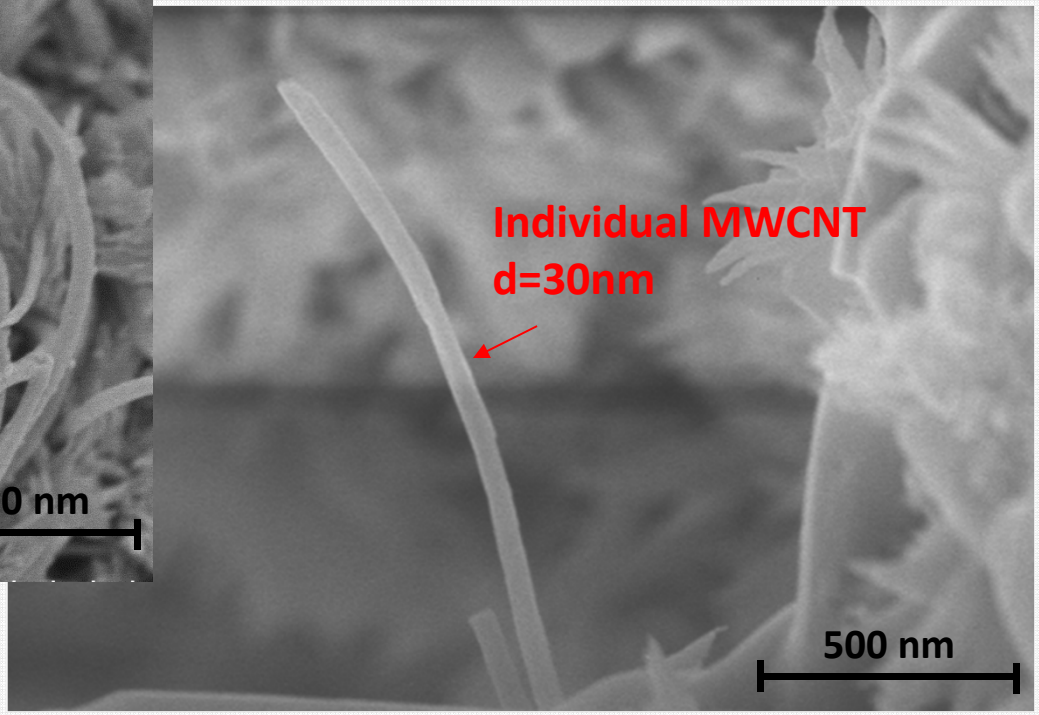
QuickTime™ and a
YUV420 codec decompressor
are needed to see this picture.

# Highly Dispersed MWCNTs

- Effective Dispersion of MWCNTs Requires Ultrasonic Energy and the Use of Surfactant (SFC)




Without Dispersion



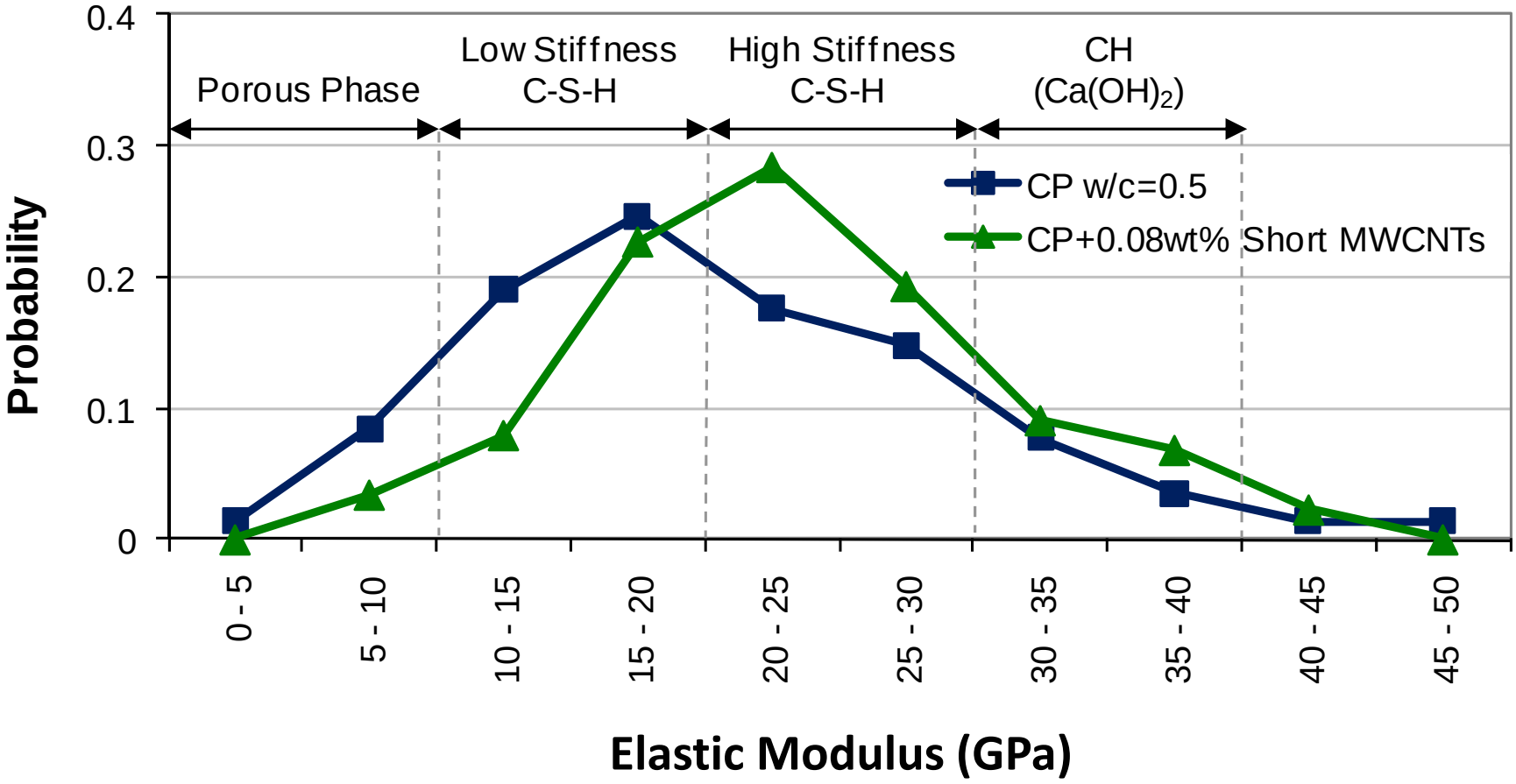

Dispersion with Sonication+Surfactant

Konsta-Gdoutos et al, Cement and Concrete Composites, 2010

Konsta-Gdoutos et al, Cement and Concrete Research, 2010

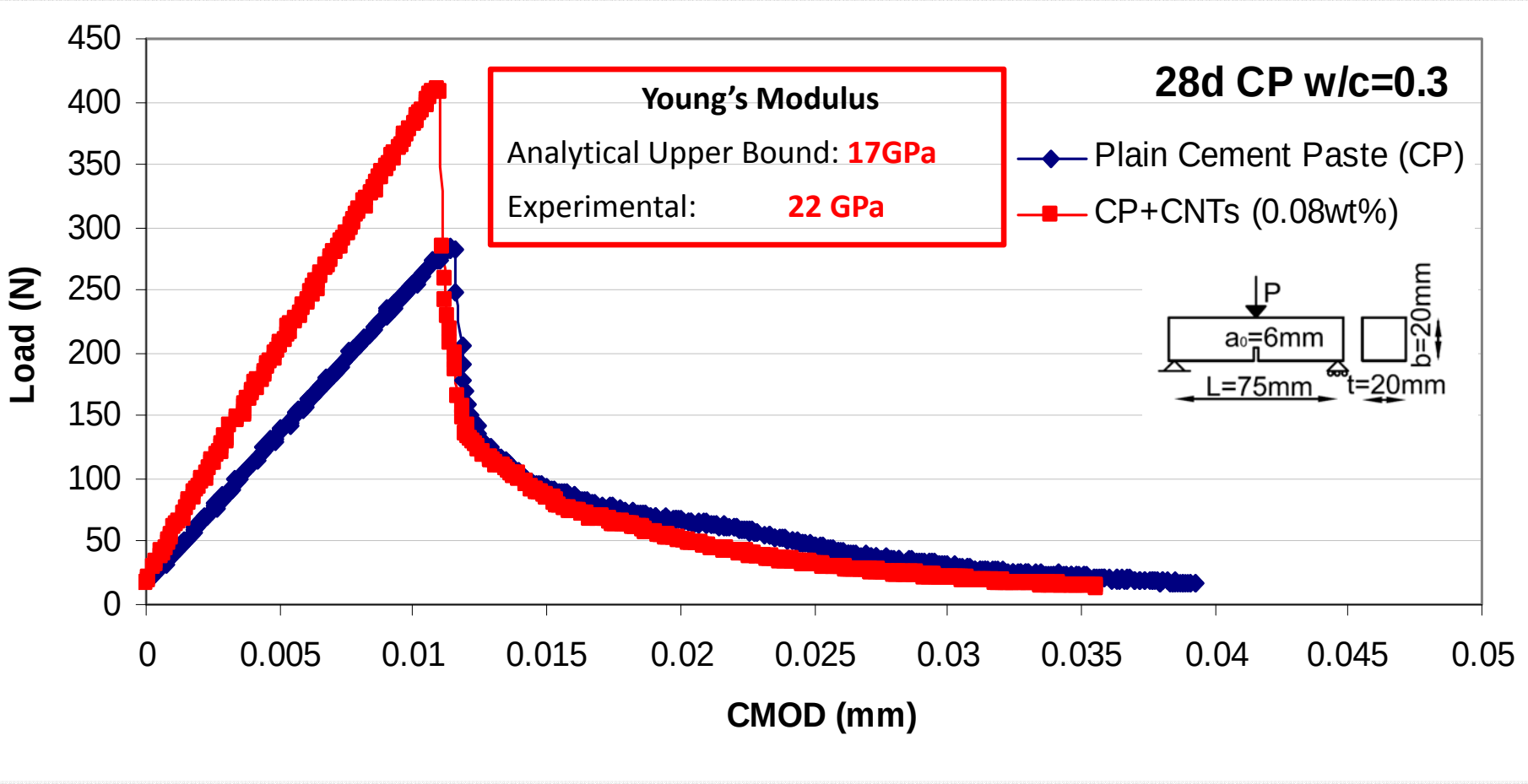
# Nanoindentation Test Results

## Elastic Modulus of Plain Cement Paste (CP) vs CP reinforced with MWCNTs



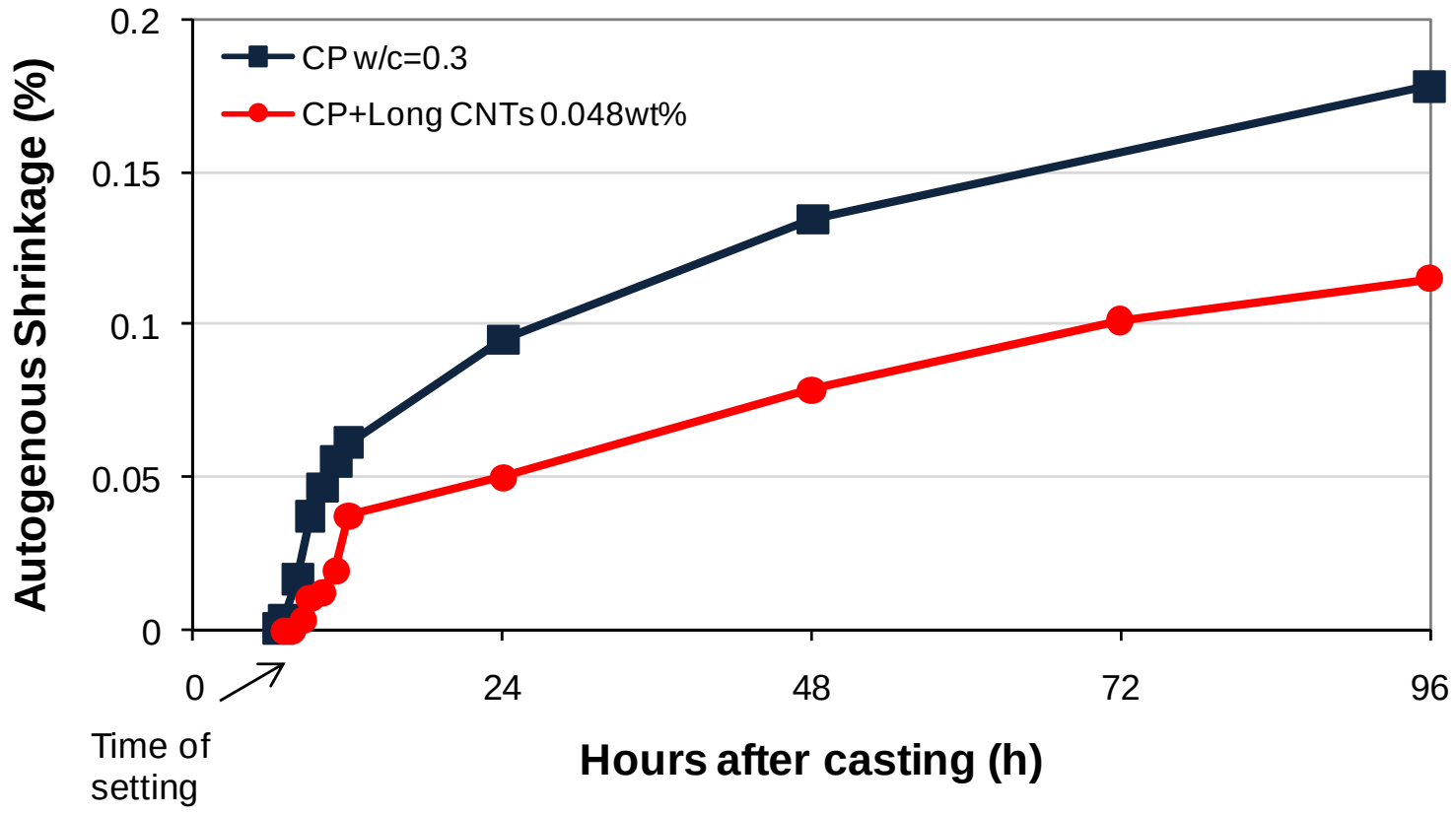

Shah et al, NICOM3, Springer, 2009

# Fracture Properties of Cement Paste Reinforced with CNTs



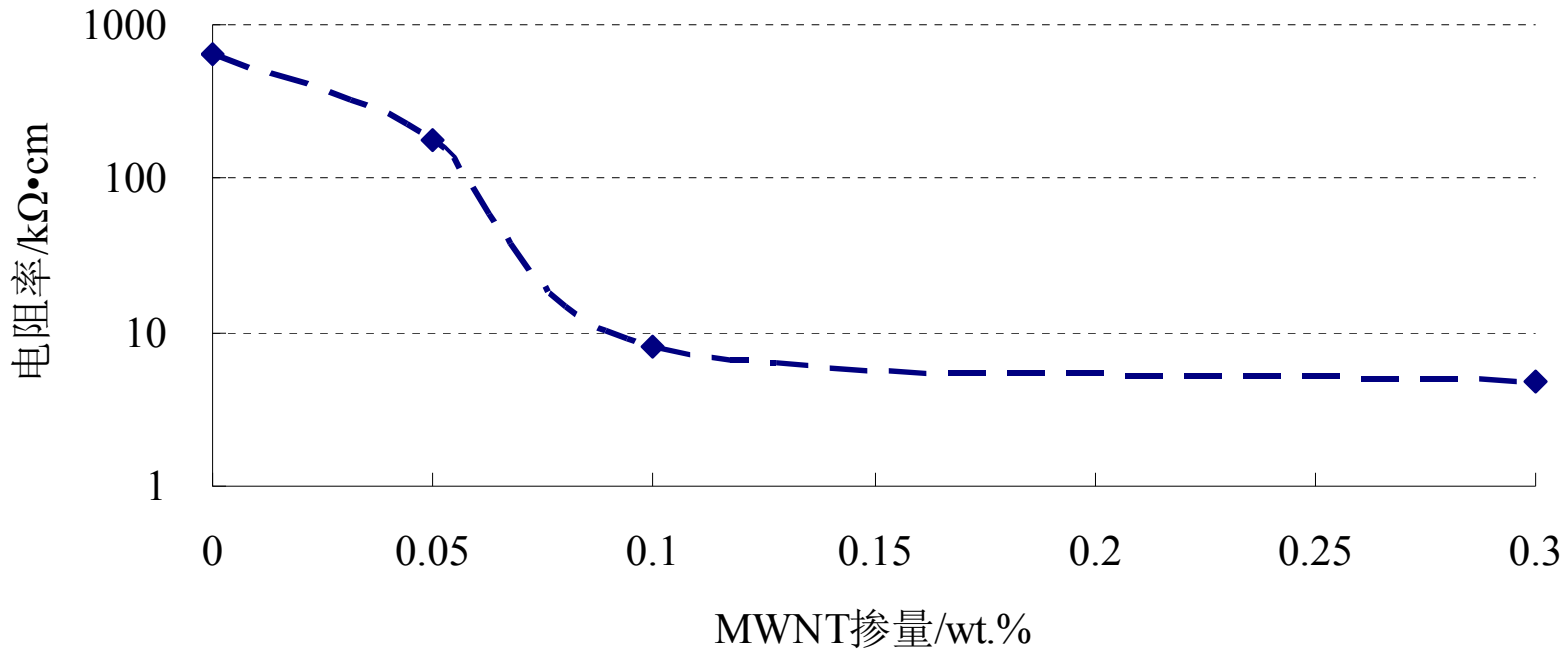

Konsta-Gdoutos et al, Cement and Concrete Composites, 2010

# Autogenous Shrinkage




Konsta-Gdoutos et al, Cement and Concrete Composites, 2010

# Conductivity

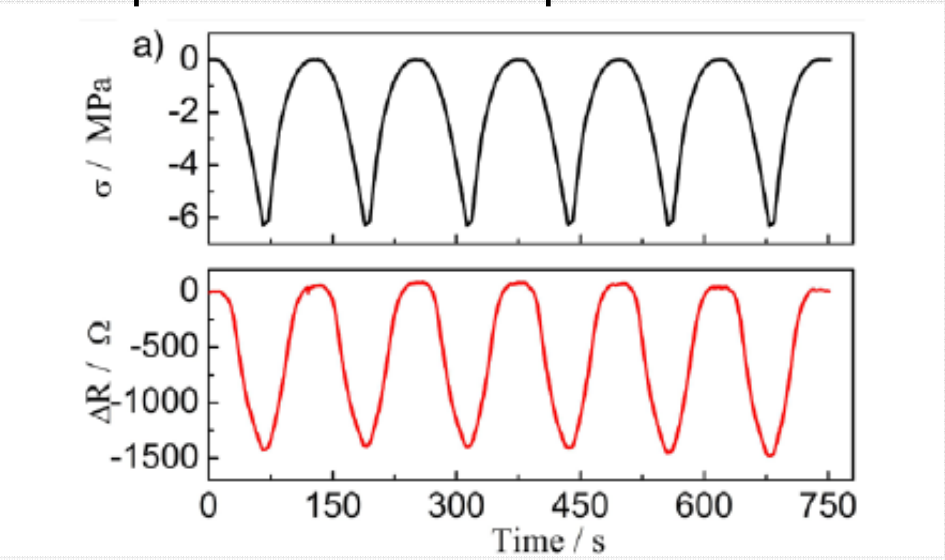


# Development of "smart" cement based materials using CNTs

Goal: Develop stress and strain sensing materials used for structural health monitoring

How?: Using Carbon nanotubes

- CNTs exhibit electromechanical properties. When subject to stress their electrical properties change analogous to the stress level indicating a linear and reversible piezoresistive response




Compressive stress and electrical resistance of cement composite with 0.1wt% MWCNTs

Han et al., Nanotechnology, 2009

# Outline

- ☑ Nanoclays in Flocculation Study
- ☑ NanoCaCO$_3$ in HVFA Cement Systems
- ☑ Nanomechanical Properties for Construction Materials
- ☑ Electrokinetic Nanoparticle (EN) Treatment for Corrosion Mitigation
- ☑ Photocatalytic Cement-Based Materials
- ☑ Carbon Nanotubes as Reinforcement and Sensors

# Conclusion

**Nanoparticles:**

Nanoclay

$NanoCaCO_3$

Nanosilica

$NanoTiO_2$

CNTs

**Nanomodification**

**Potential benefit to properties:**

Rheology

Hydration kinetics

Mechanical

C-S-H modification

Durability

Shrinkage

Photocatalysis

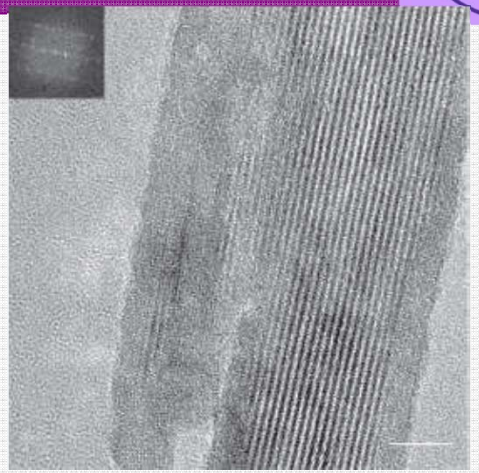
Conductivity

Piezoresistivity

# New (Old?) Materials!

- Damascus sabers contain *carbon nanotubes*, as well as *nanoscale wires of cementite*, giving them a moiré pattern (from Nov. 28 article in NY Times, photo taken by Tina Fineberg)

- Nanotubes over 400 years old!



TEM image showing nanotubes
*[Reibold et. al, 2006]*

# Thank you!