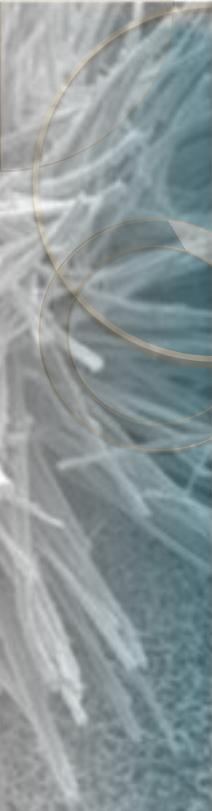




Nanotechnology

New Methods and Materials Coming to a DOT near You!!

Moderator
Don Streeter, P.E.
NY DOT

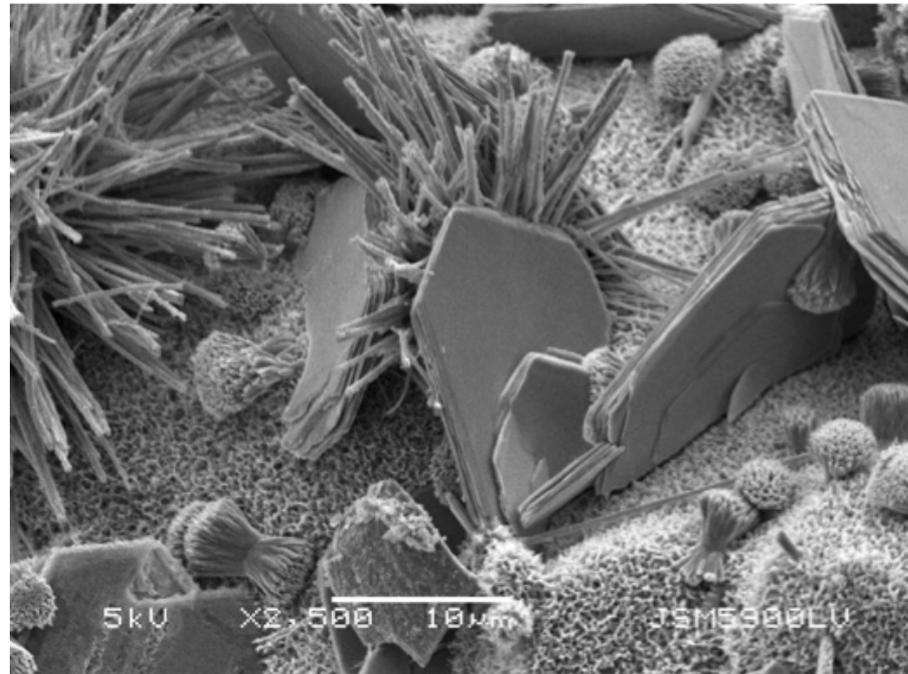


Webinar Overview

- What is Nanotechnology?
 - Georgene M. Geary, GGfGA Engineering, LLC
- How do we Categorize Materials at the Nano Level?
 - Dr. Marwa M. Hassan, Louisiana State University
- Different Areas of Improvement in Concrete Properties
 - Dr. Anol Mukhopadhyay, Texas A&M
- Applications of Nanotechnology in Transportation
 - Dr. Xiong (Bill) Yu, Case Western Reserve University

What is Nanotechnology?

Georgene M. Geary, P.E.
GGfGA Engineering, LLC



Cement Hydration at Nano Scale

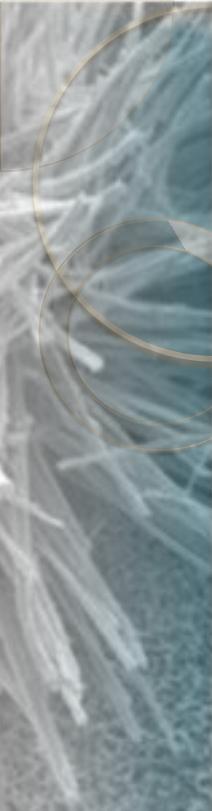
Source: Garboczi and Bentz 1995

The Nano Scale



CNT

Source: nano.gov

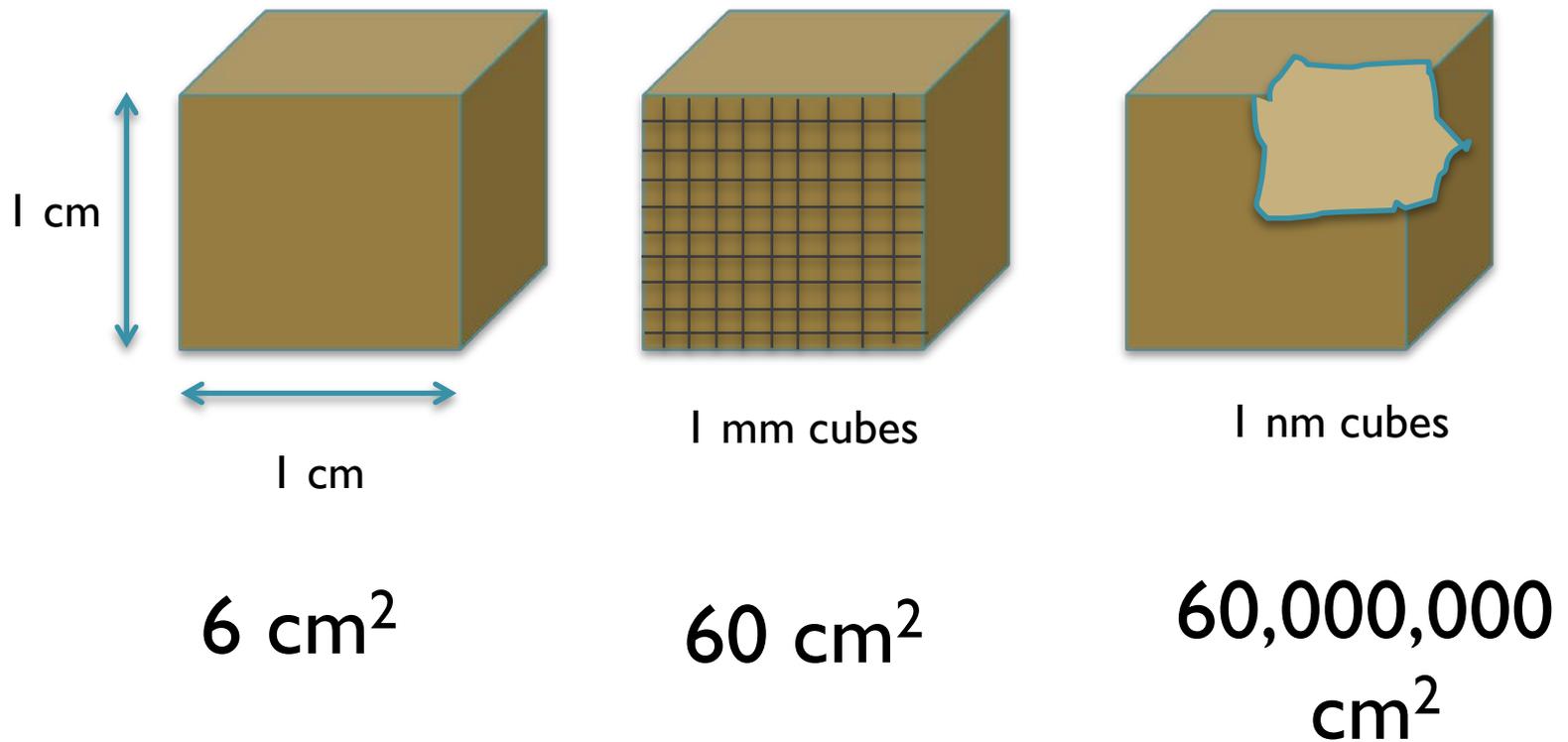


What is Nanotechnology?

- Normal Process
 - Biology and cells work at the nano scale
 - DNA is ~2 nm in diameter
- Not the Same as Normal Scale
 - Material properties can be different
 - Nano gold is red or purple

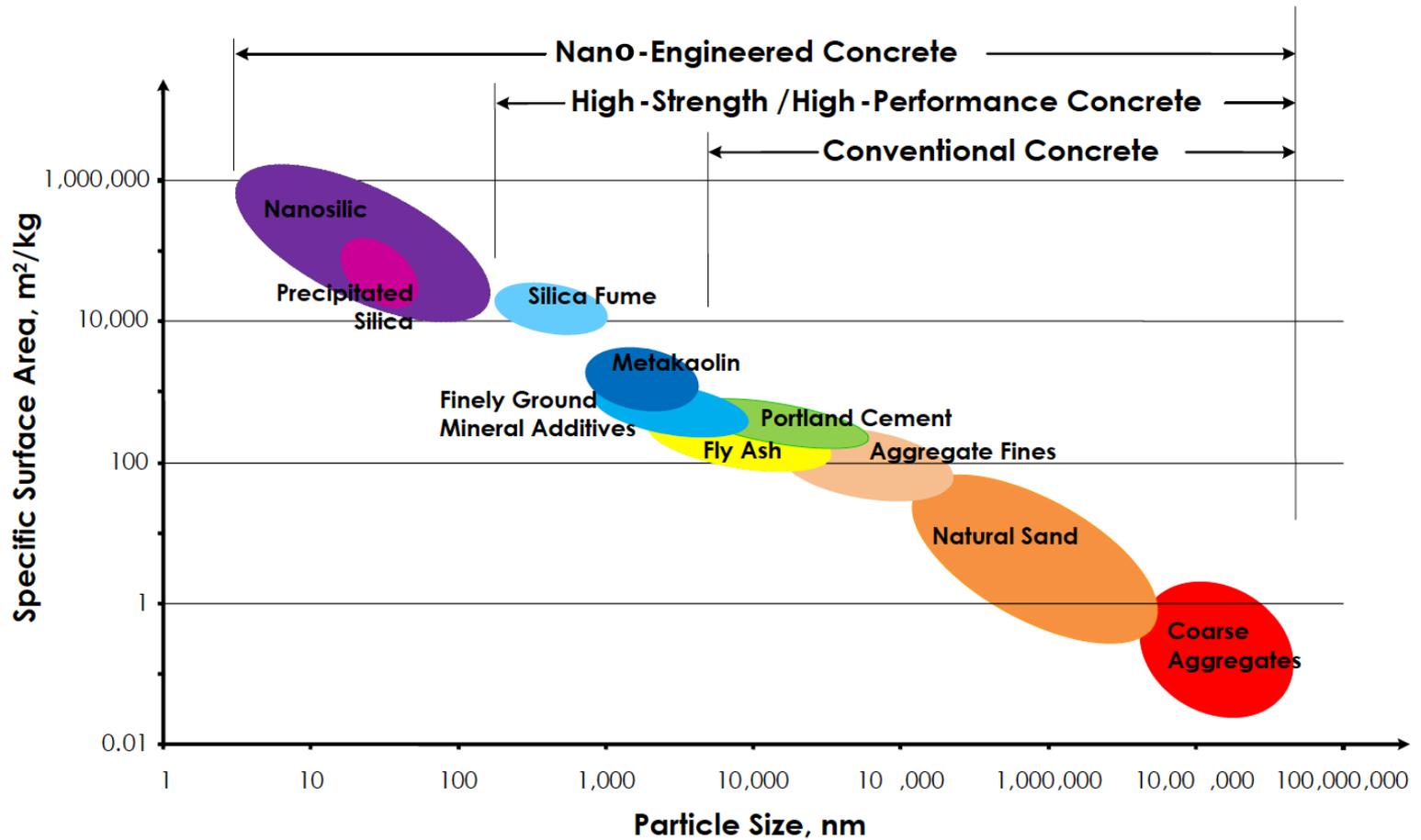
Why Nanotechnology?

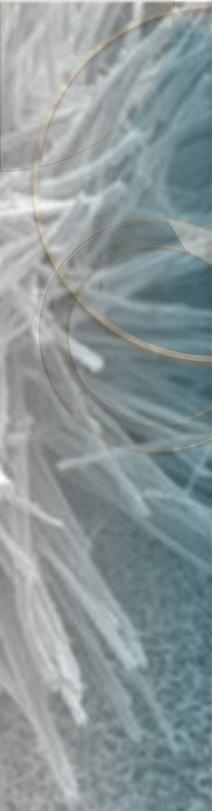
- Large Surface Area Affects



Source: nano.gov

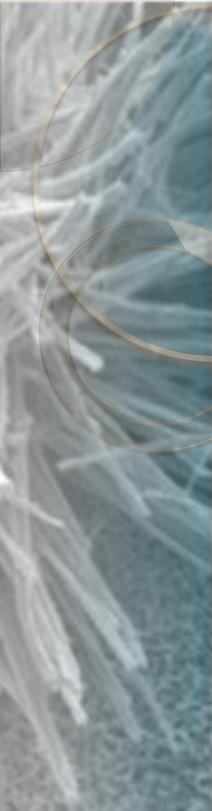
PARTICLE SIZE SCALE RELATED TO CONCRETE





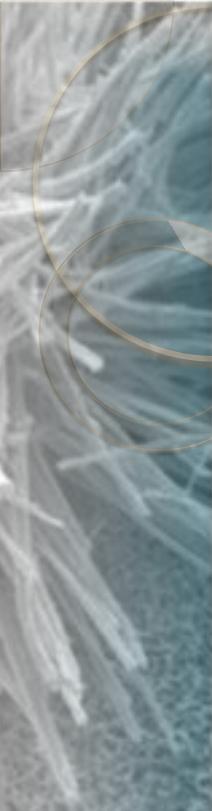
How do we use Nanotechnology?

- Adjusting/aligning material at the smallest scale (nanoscale ~ 1 -100 nanometers) to change properties
- Adding nano particles to other materials to improve properties



How will DOTs use Nanotechnology?

- Concrete Admixtures for Ultra High Performance Concrete
- Nano-sensors for Structural Monitoring
- Performance Specifications for Sustainable Materials



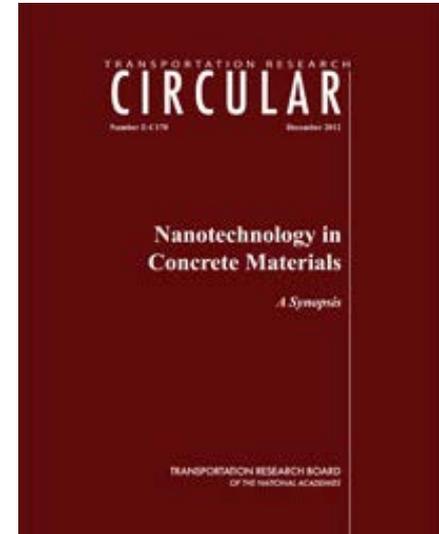
National Nanotechnology Initiative

nano.gov

- 20 Federal Agencies involved in Nano
 - USDOT/FHWA is a partner
- NNI Strategic Plan
 - FHWA Exploratory Advanced Research
 - Improve sustainability of infrastructure
- \$1.5 Billion in Presidents FY2015 Budget

To Learn More:

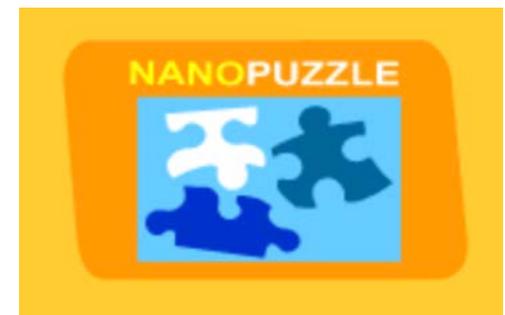
TRB E Circular 170:
Nanotechnology in Concrete
Materials: A Synopsis
(www.trb.org)



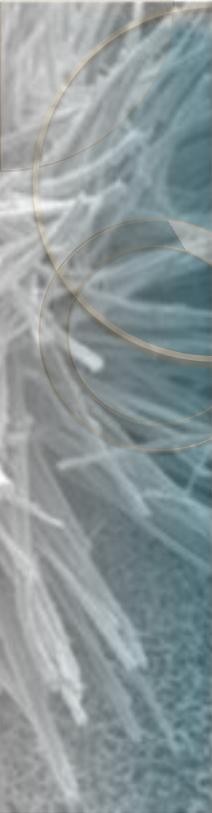
Source: www.trb.org

nanowerk.com

nanozone.org



Source: www.nanozone.org



Summary

- Nanotechnology is the science and engineering of really small things
- If we can't see it how do we engineer it?
 - Next presentations will cover this and more!



How Do We Characterize
Materials at the Nano Level?

Dr. Marwa Hassan
Louisiana State University



How Do We Characterize Materials at the Nano Level?

Nano-Scale Characterization

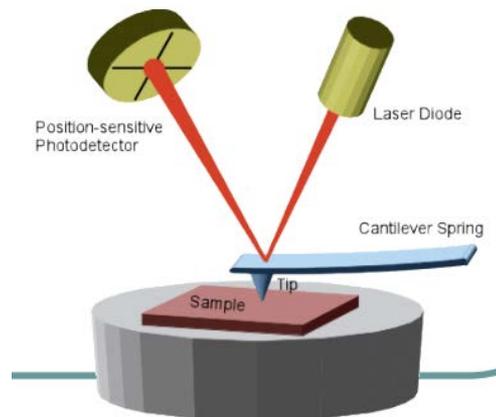
Atomic Force Microscopy

Nanoindentation

Electron Microscopy (SEM & TEM)

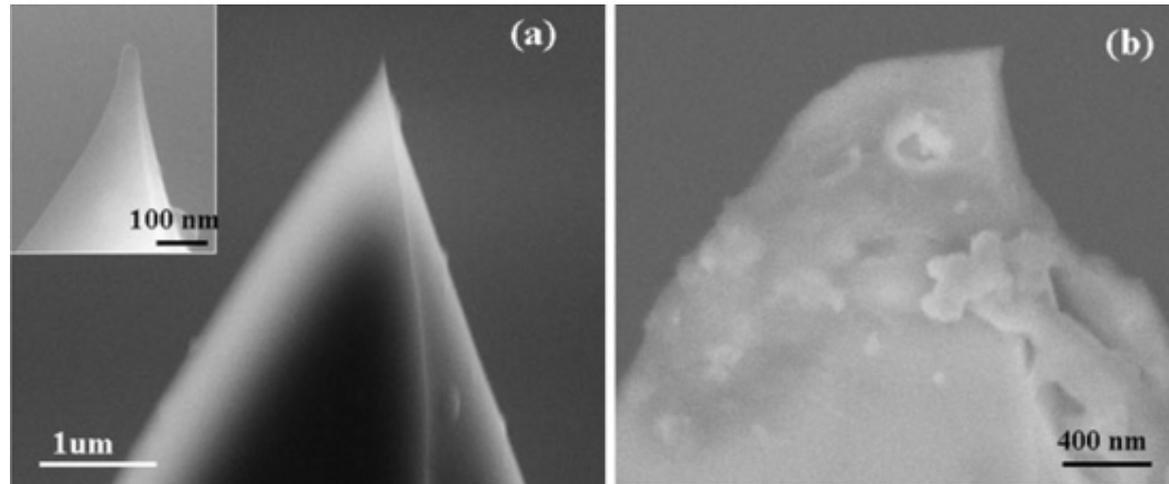
Atomic Force Microscopy (AFM)

- AFM is one type of scanning probe microscopes (SPM) introduced in 1985 by Gerd Binnig and Christoph Gerber
 - Creates images of surfaces using a probe
- The probe is moved (scanned) across the surface
- The AFM senses interatomic forces that occur between the probe tip and the substrate



Atomic Force Microscopy (AFM)

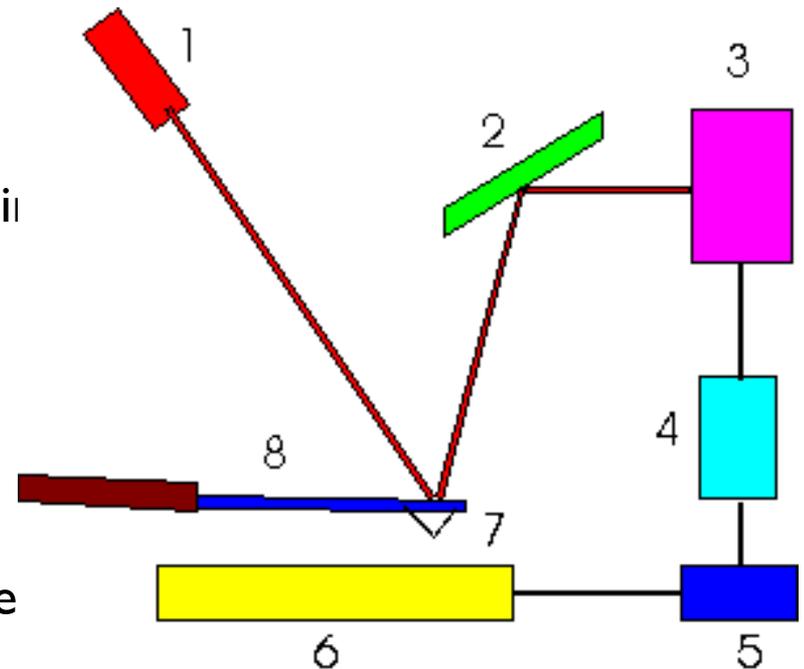
- AFMs operate by measuring force between the probe and the sample
- The probe is a sharp tip, which is a 3-6 μm tall pyramid with 15-40 nm end radius



A new AFM tip and a used AFM tip
(Figure by Wenjie Mai)

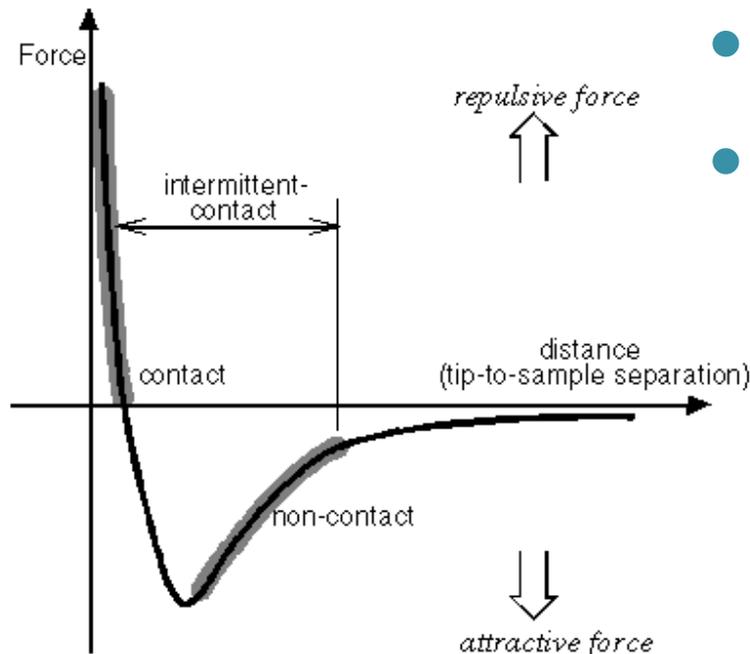
Components of AFM

1. **Laser** – deflected off cantilever
2. **Mirror** – reflects laser beam to photodetector
3. **Photodetector** – dual element photodiode that measures differences in light intensity and converts to voltage
4. **Amplifier**
5. **Register**
6. **Sample**
7. **Probe** – tip that scans sample made of Si
8. **Cantilever** – moves as scanned over sample and deflects laser beam.



Modes of Operation

- Contact Mode
- Non-Contact Mode
- Tapping (Intermittent contact) Mode



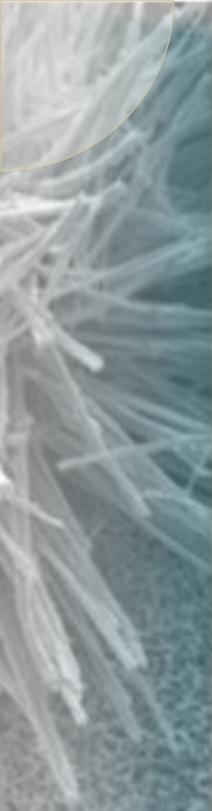
Modes of Operation

Contact Mode

- Measures repulsion between tip and sample
- Force of tip against sample remains constant
- Feedback regulation keeps cantilever deflection constant
- Voltage required indicates height of sample
- Problems: excessive tracking forces applied by probe to sample

Non-Contact Mode

- Measures attractive forces between tip and sample
- Tip doesn't touch sample
- Van der Waals forces between tip and sample detected
- Problems: Can't use with samples in fluid
- Used to analyze semiconductors
- Doesn't degrade or interfere with sample- better for soft samples



Tapping Mode

- Tip vertically oscillates between contacting sample surface and lifting of at frequency of 50,000 to 500,000 cycles/sec.
- Oscillation amplitude reduced as probe contacts surface due to loss of energy caused by tip contacting surface
- Advantages: overcomes problems associated with friction, adhesion, electrostatic forces
- More effective for larger scan sizes

Advantages and Disadvantages of AFM

Advantages

- Easy sample preparation
- Accurate height information
- Works in vacuum, air, and liquids
- Living systems can be studied

Disadvantages

- Images are not ideally sharp
- Limited vertical range
- Limited magnification range
- Data not independent of tip
- Tip or sample can be damaged

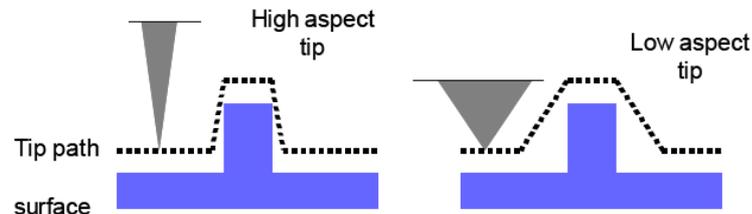
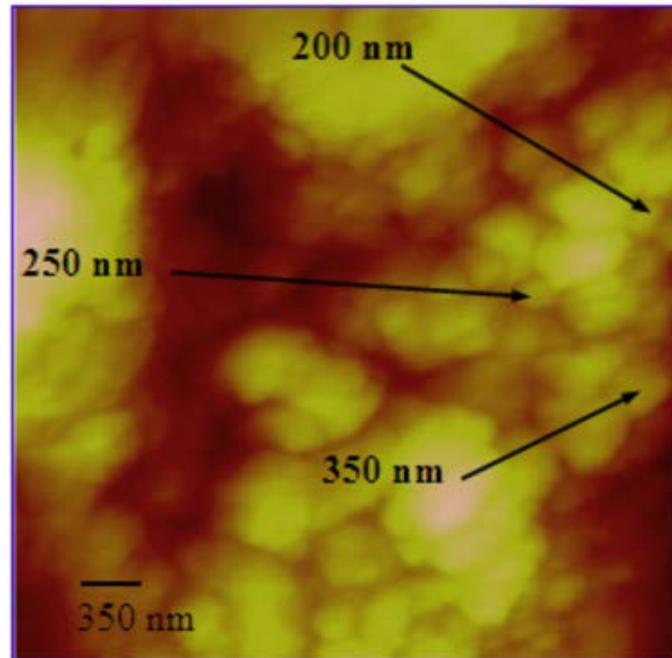


Figure 6. Ideally a probe (tip) with a high aspect ratio will give the best resolution. The radius of curvature of the probe leads to tip convolution. This does not often influence the height of a feature but the lateral resolution.

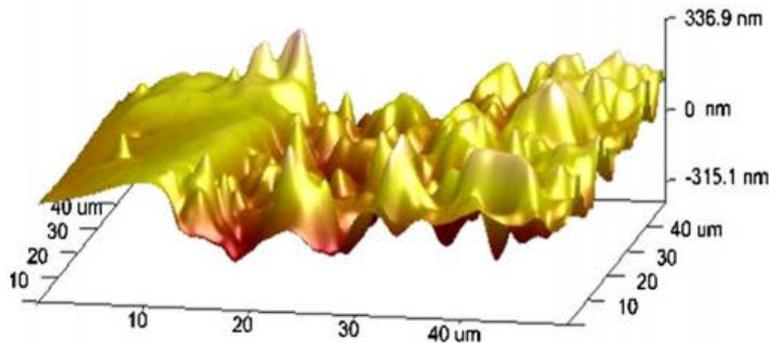
Applications of AFM in Concrete Materials

- **Cement:** Used to detect level of hydration and effects of supplementary cementitious materials (fly ash, silica fume, etc.)

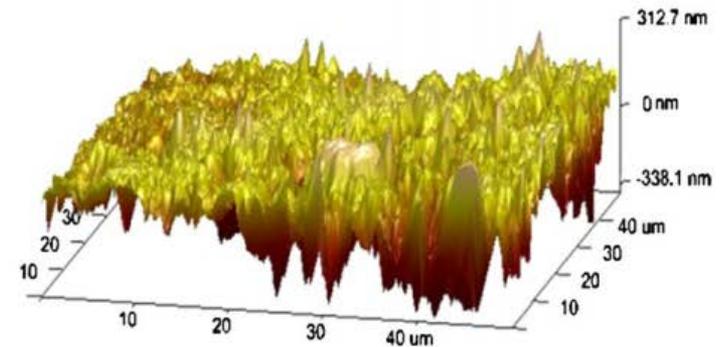


Atomic Force Microscopy (AFM)

- AFM used in Recycled Aggregate Concrete (RAC) research to investigate surface roughness of old and new Interfacial Transition Zones (ITZs).

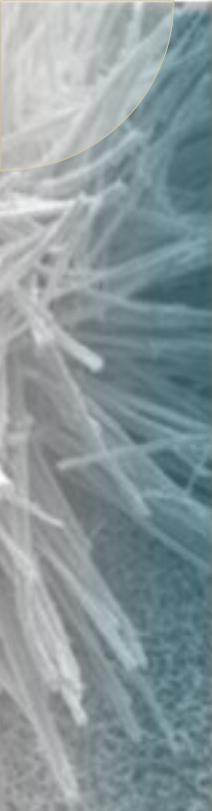


(a) Old ITZ (50×50μm)



(b) New ITZ (50×50μm)

Typical AFM 3D topography image of ITZ in RAC (Image by Xiao et al)

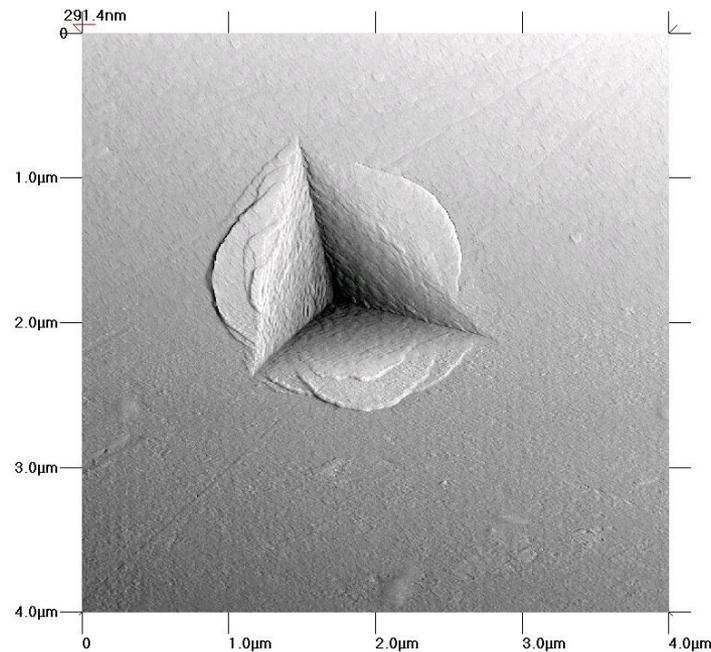


Nanoindentation

- ***An indentation test*** consists of touching a material of interest whose mechanical properties such as elastic modulus and hardness are unknown with another material whose properties are known
- ***Definition of Nanoindentation:*** Mechanical probing of a material surface to nm-scale depths, while simultaneously monitoring LOAD and DEPTH.

Nanoindentation

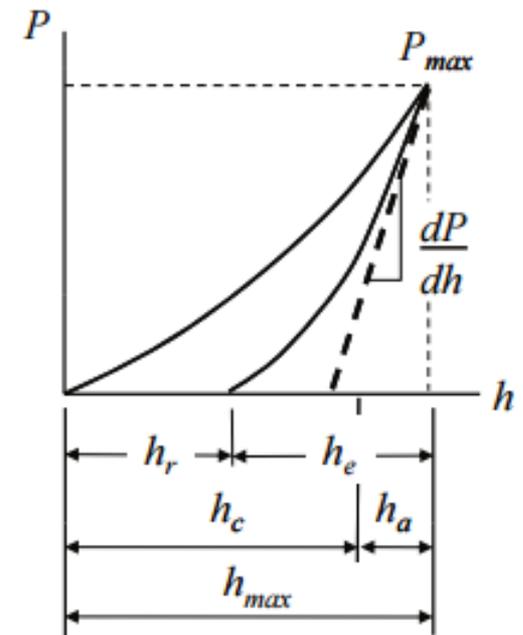
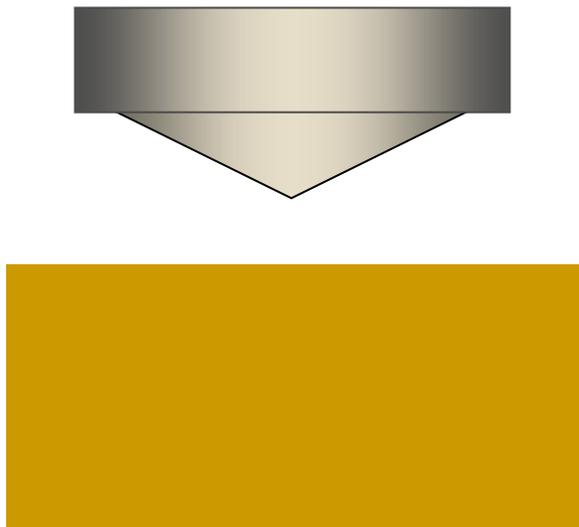
- Nanoindentation is an indentation test in which the length scale of the penetration is measured in nanometers.



An AFM image of the residual indent left during a nanoindentation experiment on a Zr-Cu-Al metallic glass (Image by Jonathan Puthoff, University of Wisconsin – Madison).

Nanoindentation

- From the nanoindentation test, the elastic modulus and hardness of the specimen material can be estimated from load-displacement measurements



Load vs. depth of penetration curve during loading and unloading cycle
(Figure by Fischer-Cripps, Nanoindentation).

Nanoindentation Measurements

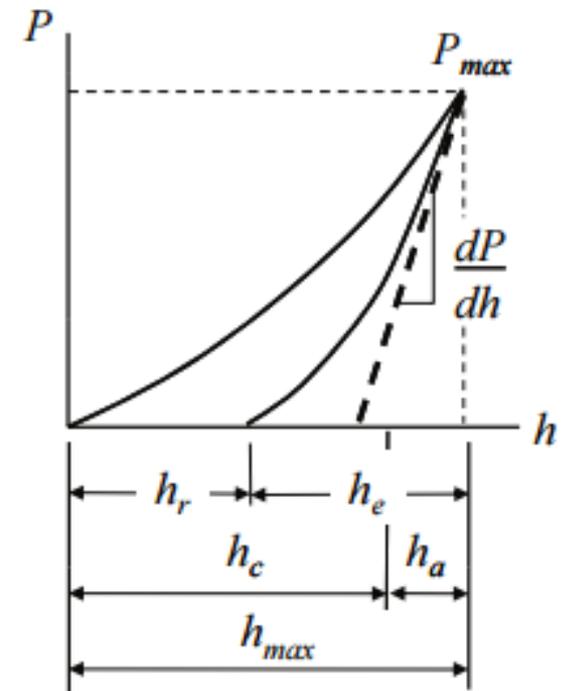
- The depth of the contact circle h_c and slope of elastic unloading at maximum load dP/dh allow specimen modulus and hardness to be calculated

$$E^* = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} \frac{dP}{dh}$$

Indentation modulus

$$H = \frac{P}{A}$$

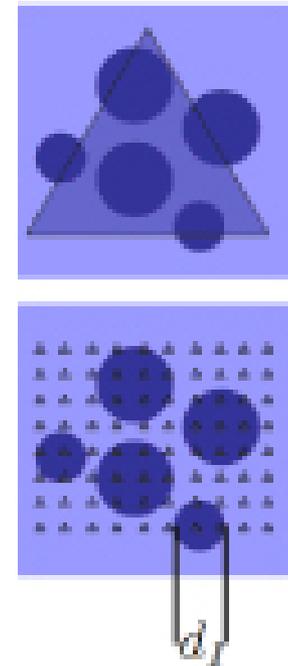
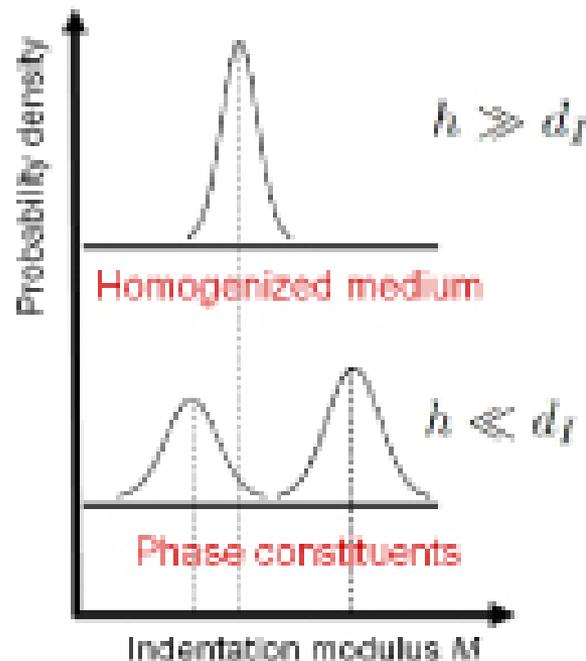
Indentation hardness



Load vs. depth of penetration curve during loading and unloading cycle (Figure by Fischer-Cripps, Nanoindentation)

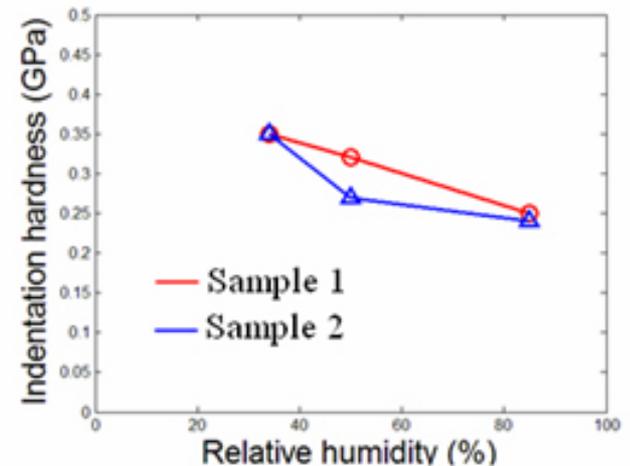
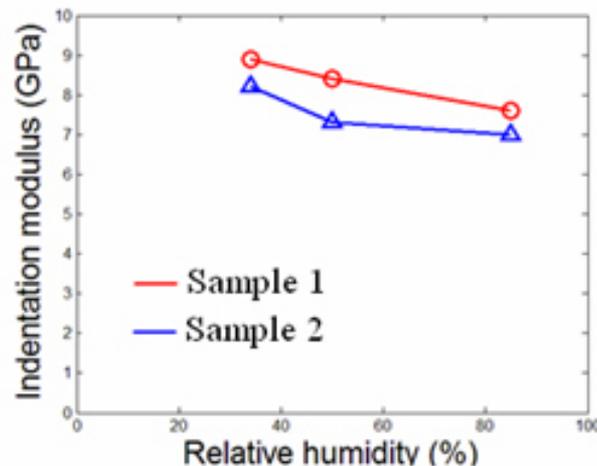
Applications of Nanoindentation in Concrete

- **Cement:** Using grid indentation technique, heterogeneous properties of C-S-H can be measured for different phases



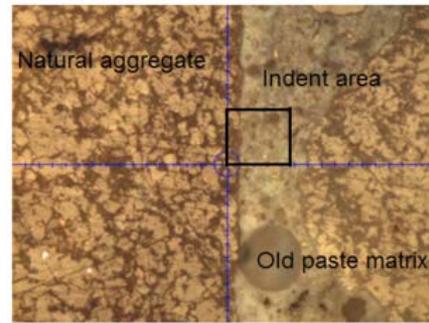
Applications of Nanoindentation in Concrete

- **Cement:** the indentation penetration depth must remain significantly smaller than the phase size
- Effect of relative humidity on modulus and hardness

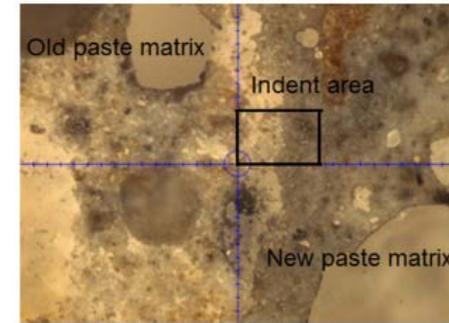


Applications of Nanoindentation in Concrete

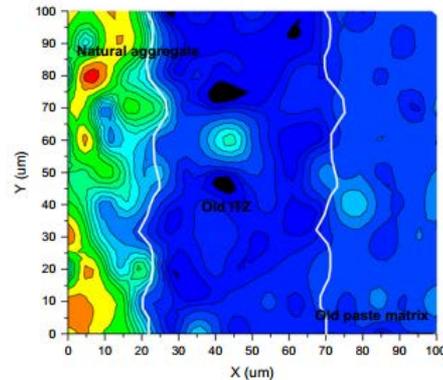
- Nanoindentation used in Recycled Aggregate Concrete (RAC) research to investigate mechanical properties of old and new Interfacial Transition Zones (ITZs)



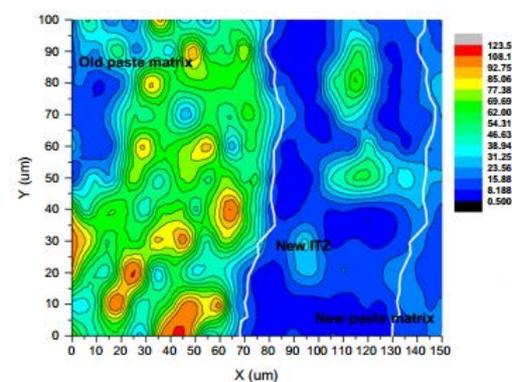
(a) Old ITZ, indent area: 100x100 μm



(b) New ITZ, indent area: 150x100 μm



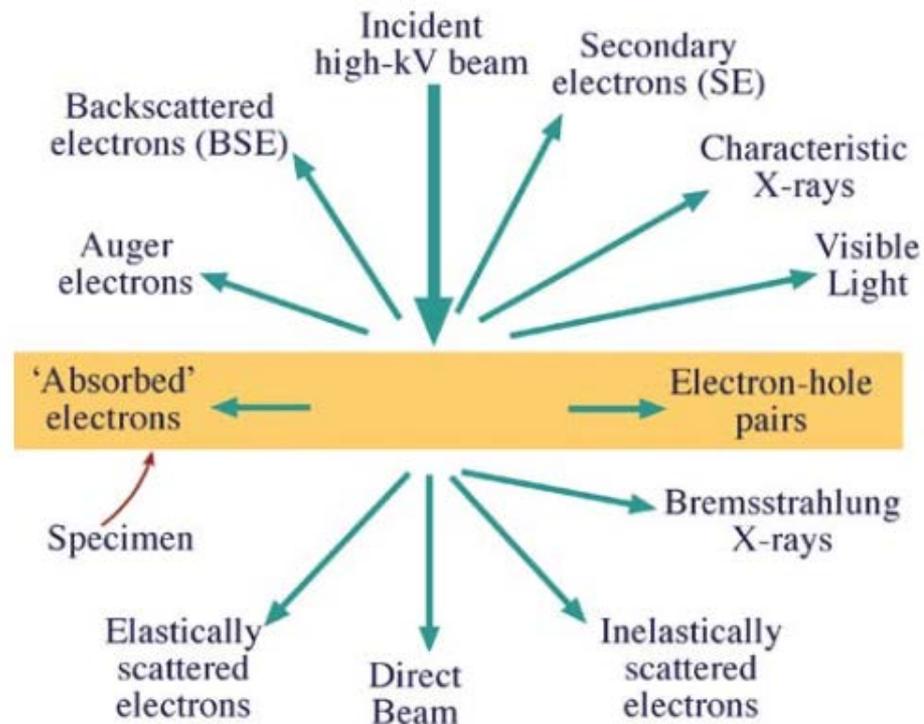
(c) Contour map of modulus in GPa (old ITZ)



(d) Contour map of modulus in GPa (new ITZ)

Electron Microscopy (SEM & TEM)

- Electron microscopy is a technique based on the interaction between an electron beam and a sample.



Electron Microscopy (SEM and TEM)

The signals that derive from electron-sample interaction reveal information about the sample including (Swapp, University of Wyoming):

- External morphology, texture (Secondary Electrons, SE)
- Chemical composition (Characteristic X-Ray, EDS)
- Crystalline structure and orientation of materials making up the sample (Backscattered and diffracted backscattered electrons)

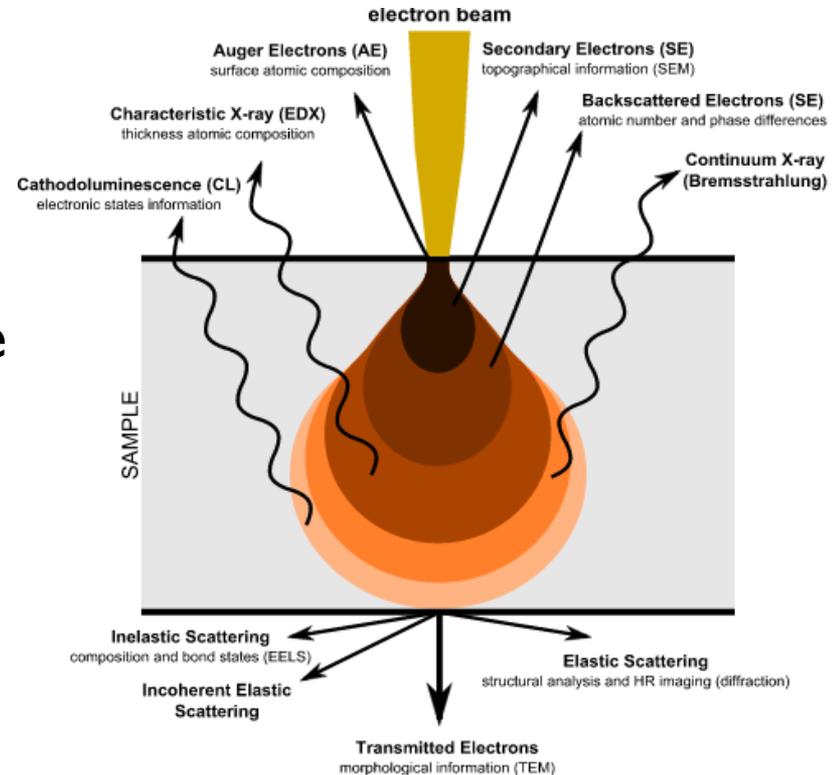
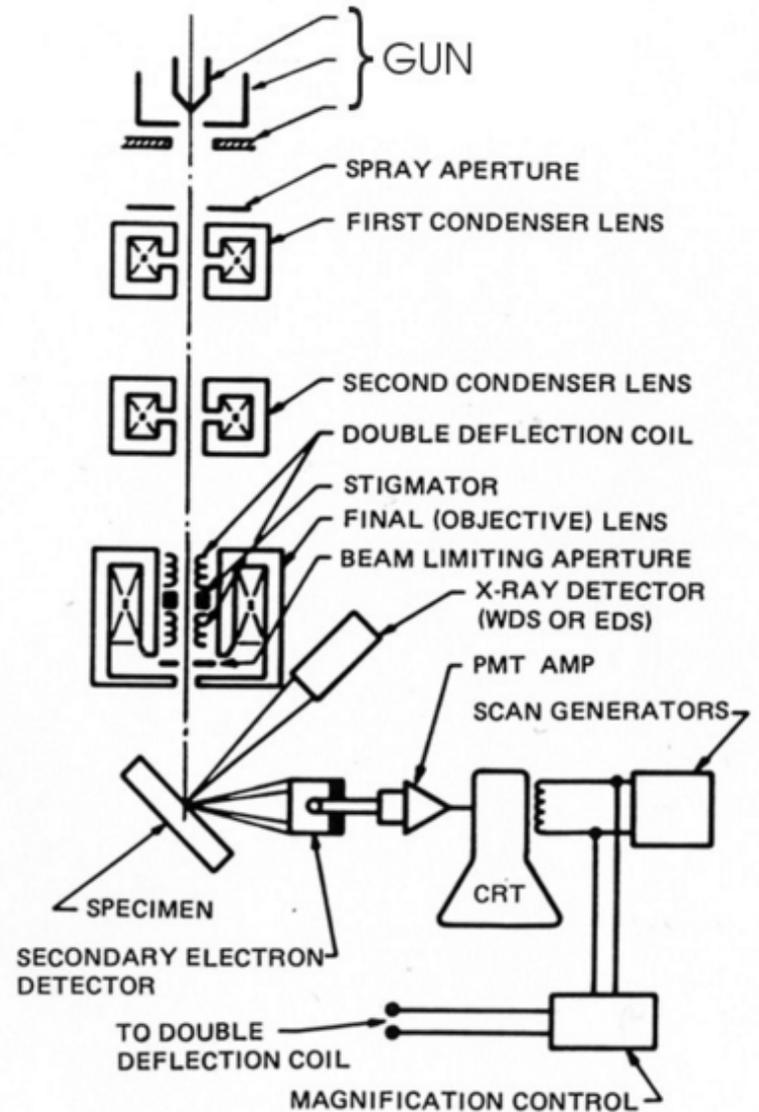


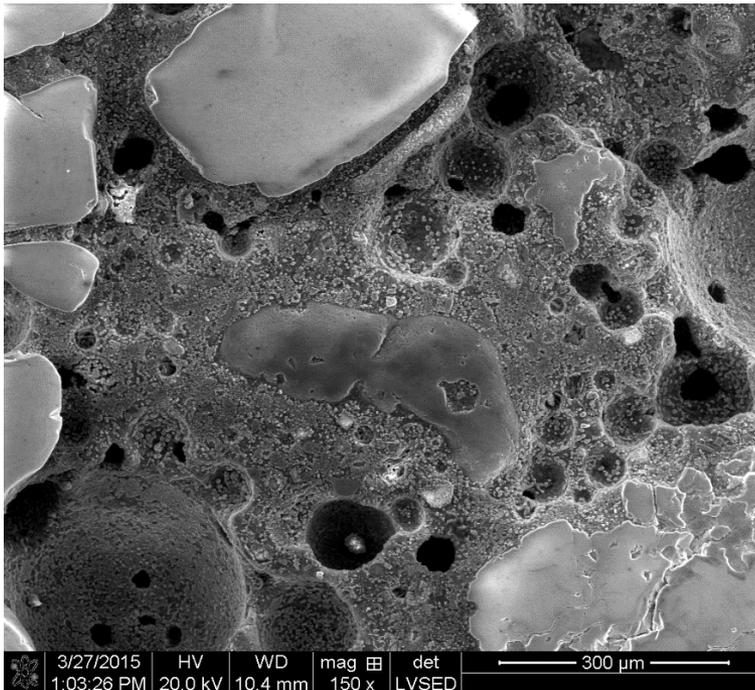
Figure by Claudionico

Scanning Electron Microscopy (SEM)

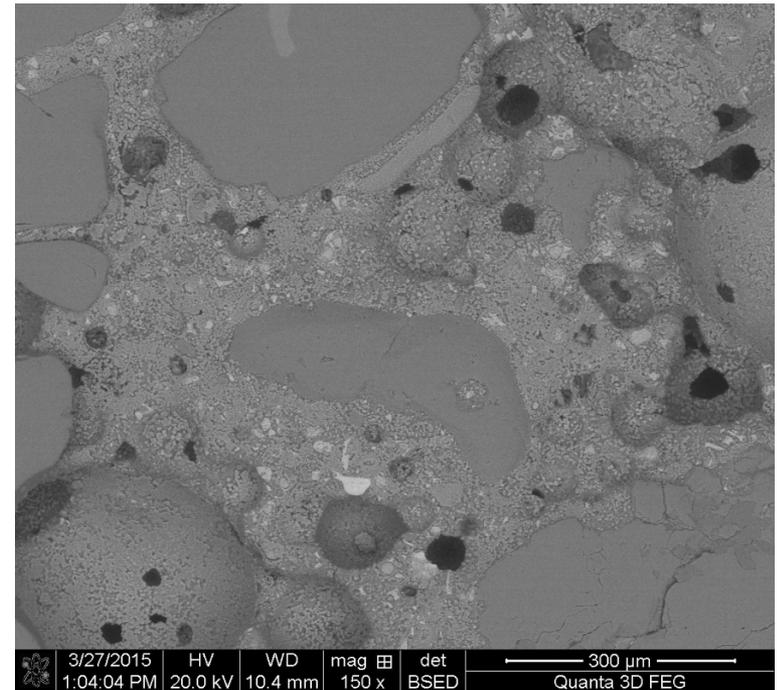


Scanning Electron Microscopy (SEM)

- SEM magnification ranges from 20x to approximately 30,000x with a spatial resolution of 50 to 100 nm
- SEM can provide us with SE and BSE (Z contrast) images.



SE Image of concrete specimen



BSE Image of concrete specimen

Scanning Electron Microscopy (SEM)

SEM can also provide us with:

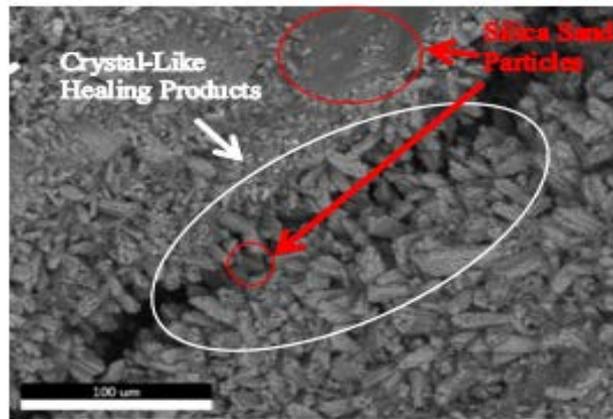
- Localized chemical composition by utilizing Energy Dispersive Spectroscopy (EDS).



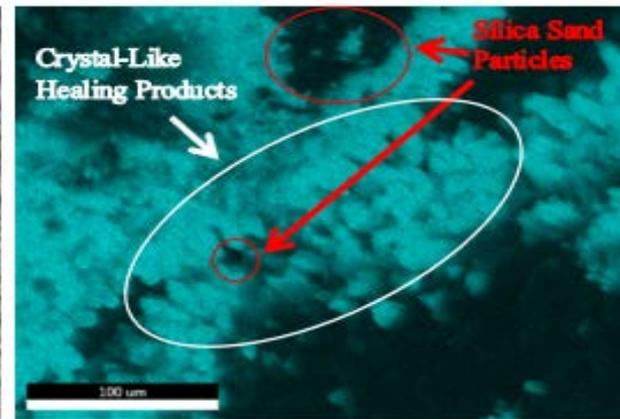
EDS and EBSD equipment (Image by EDAX)

Scanning Electron Microscopy (SEM)

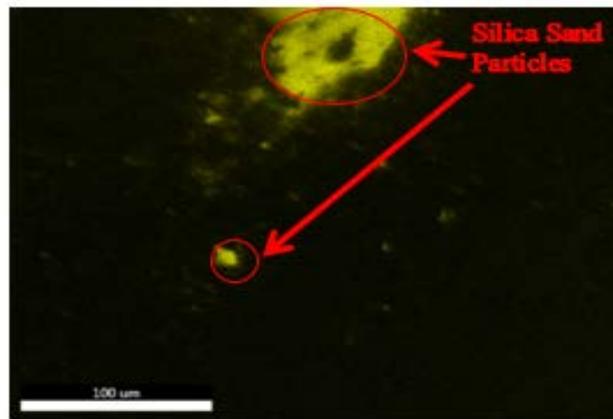
- SEM-EDS utilized in self-healing concrete research to characterize healing products



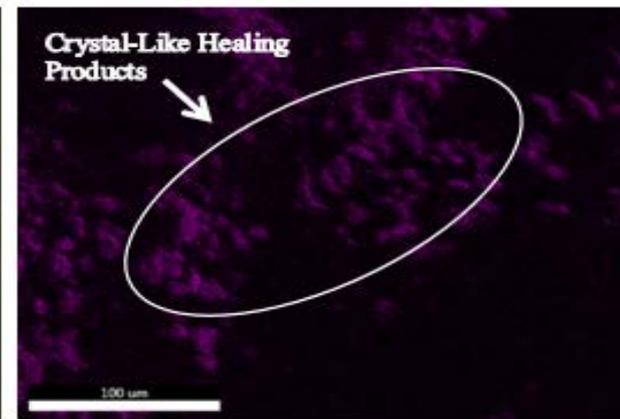
BSE image



Ca distribution map



Si distribution map

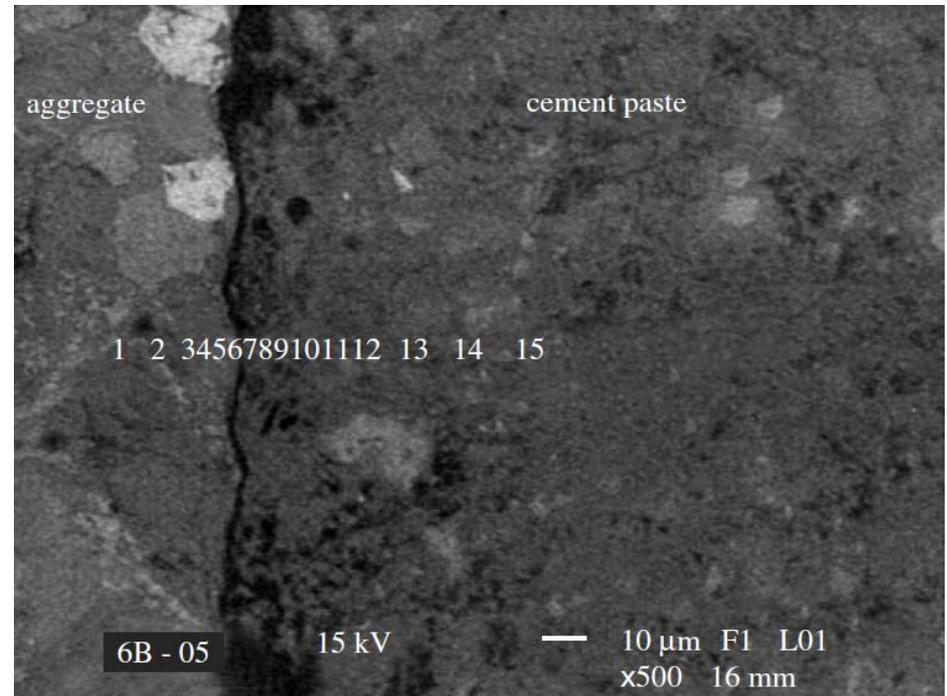
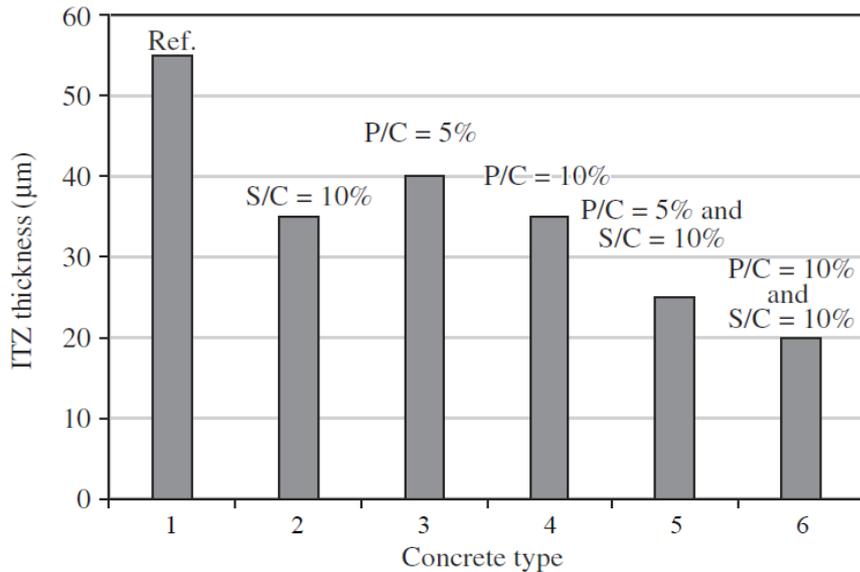
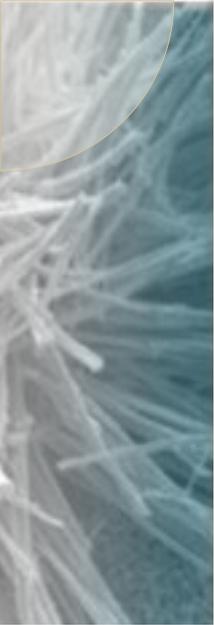


C distribution map

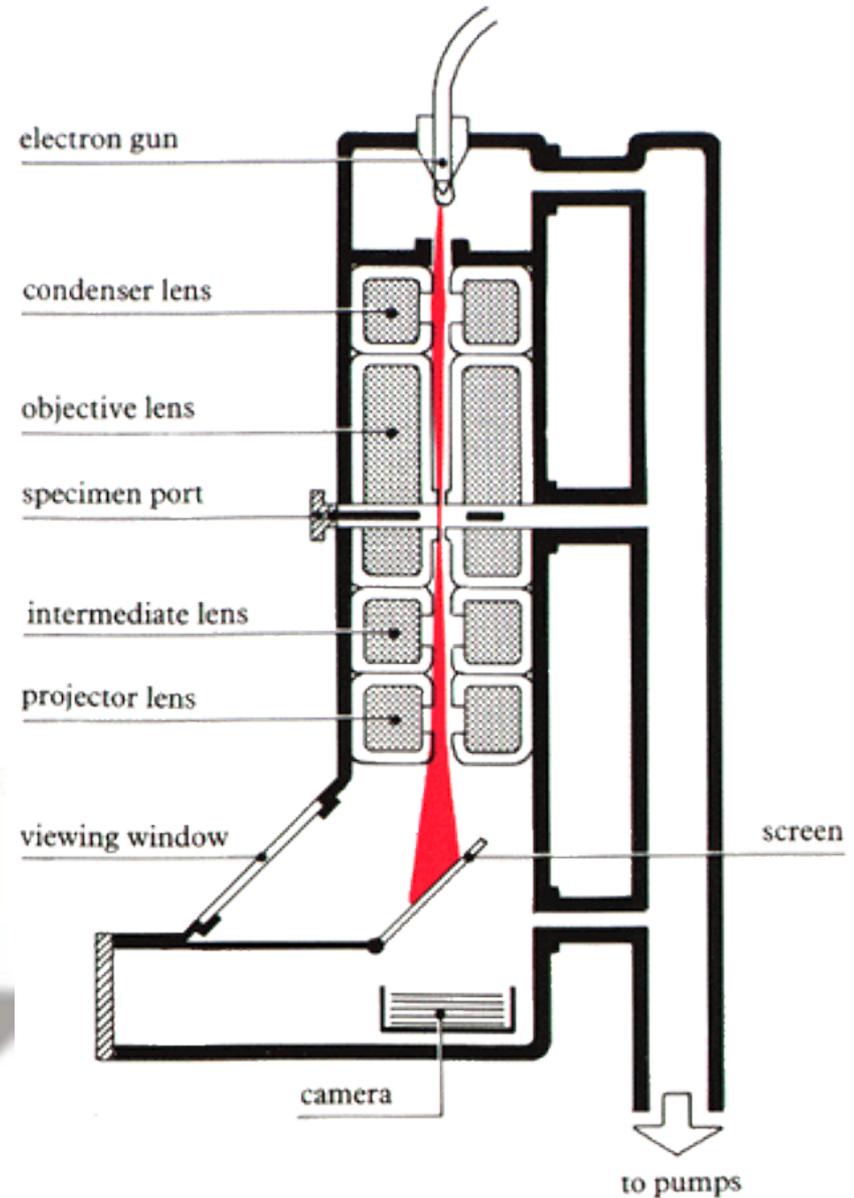
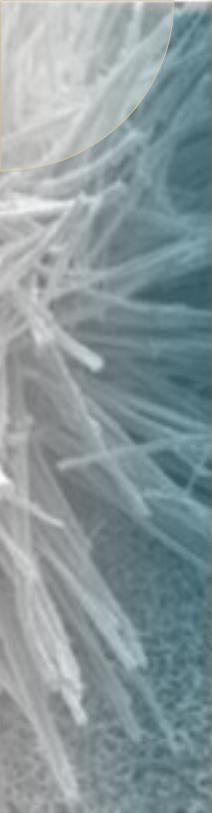
EDS
elemental
distribution
maps
(Image by
Arce et al)

Scanning Electron Microscopy (SEM)

- Scanning Electron Microscope (SEM) equipped with energy dispersive x ray analysis system (EDX) was utilized to study the microstructure of the interfacial transitional zone (ITZ) and its thickness

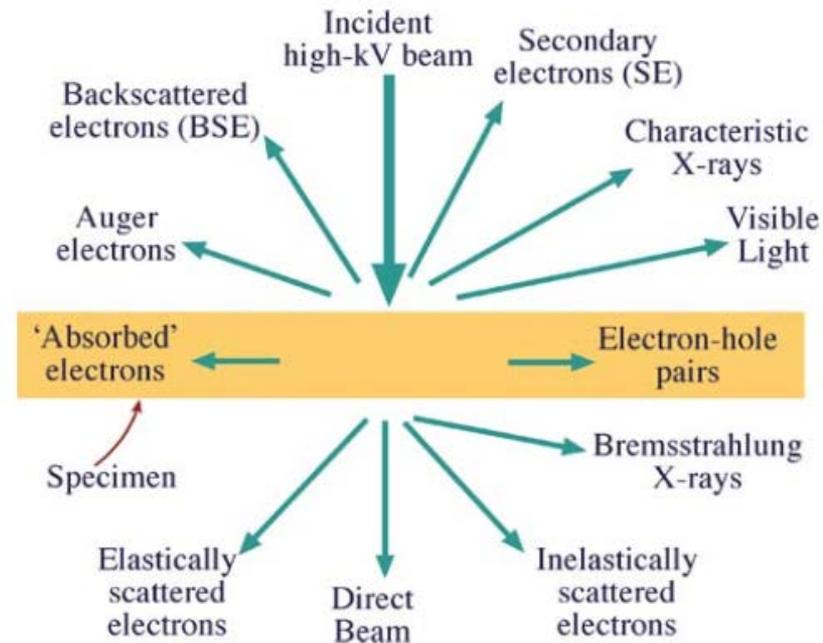


Transmission Electron Microscopy (TEM)



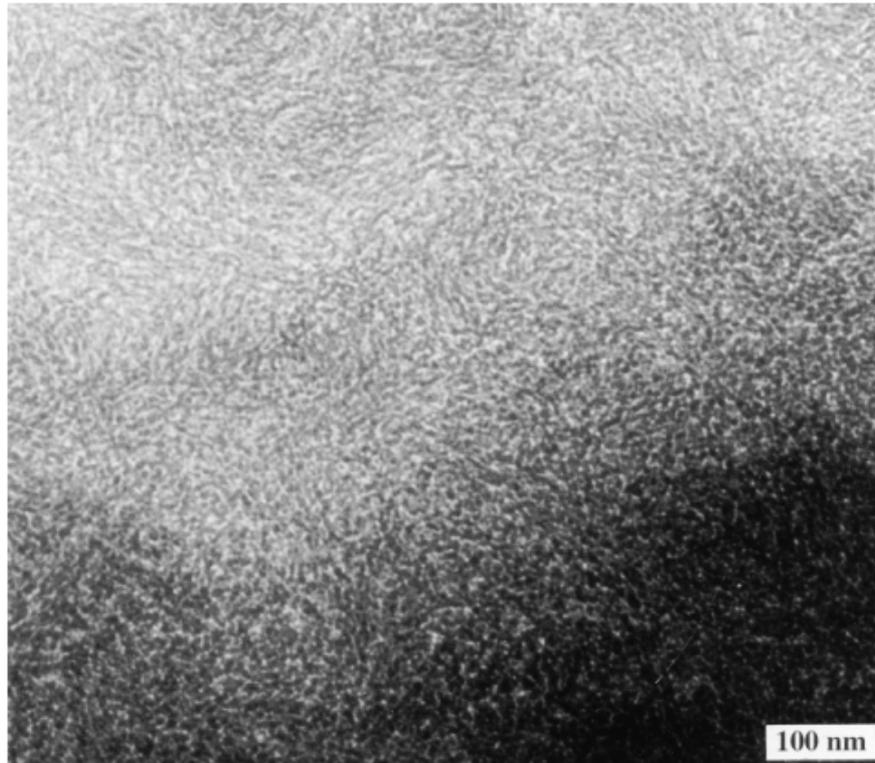
Transmission Electron Microscopy (TEM)

- Requires thin, electron transparent, specimens (100 – 500 nm thick).
- The electron beam is transmitted through the thin specimen and interacts with it as it passes through.
- The interaction between the transmitted electron beam and the thin specimen generates signals which allows for an image to be generated.

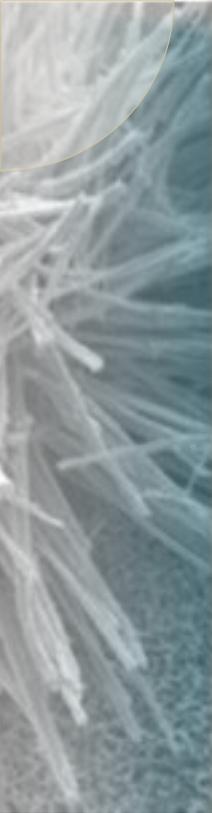


Transmission Electron Microscopy (TEM)

- TEM utilized to study the nanostructure of calcium silicate hydrates (C-S-H) in concrete.



TEM image of CSH in Portland Cement Paste (Figure by I.G.Richardson)



References

- Anthony C. Fischer-Cripps, Nanoindentation, Springer, 2002
- Jianzhuang Xiao, Wengui Li, Zhihui Sun, David A. Lange, Surendra P. Shah, Properties of interfacial transition zones in recycled aggregate concrete tested by nanoindentation, *Cement & Concrete Composites* 37 (2013)
- Wenjie Mai, *Fundamental Theory of Atomic Force Microscopy*, <http://www.nanoscience.gatech.edu/ziwang/research/afm.html>
- Susan Swapp, *Scanning Electron Microscopy (SEM)*, University of Wyoming, http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html
- David B. Williams, C. Barry Carter, *Transmission Electron Microscopy*, Springer, 2009
- I.G. Richardson, The nature of C-S-H in hardened cements, *Cement and Concrete Research* 29 (1999)

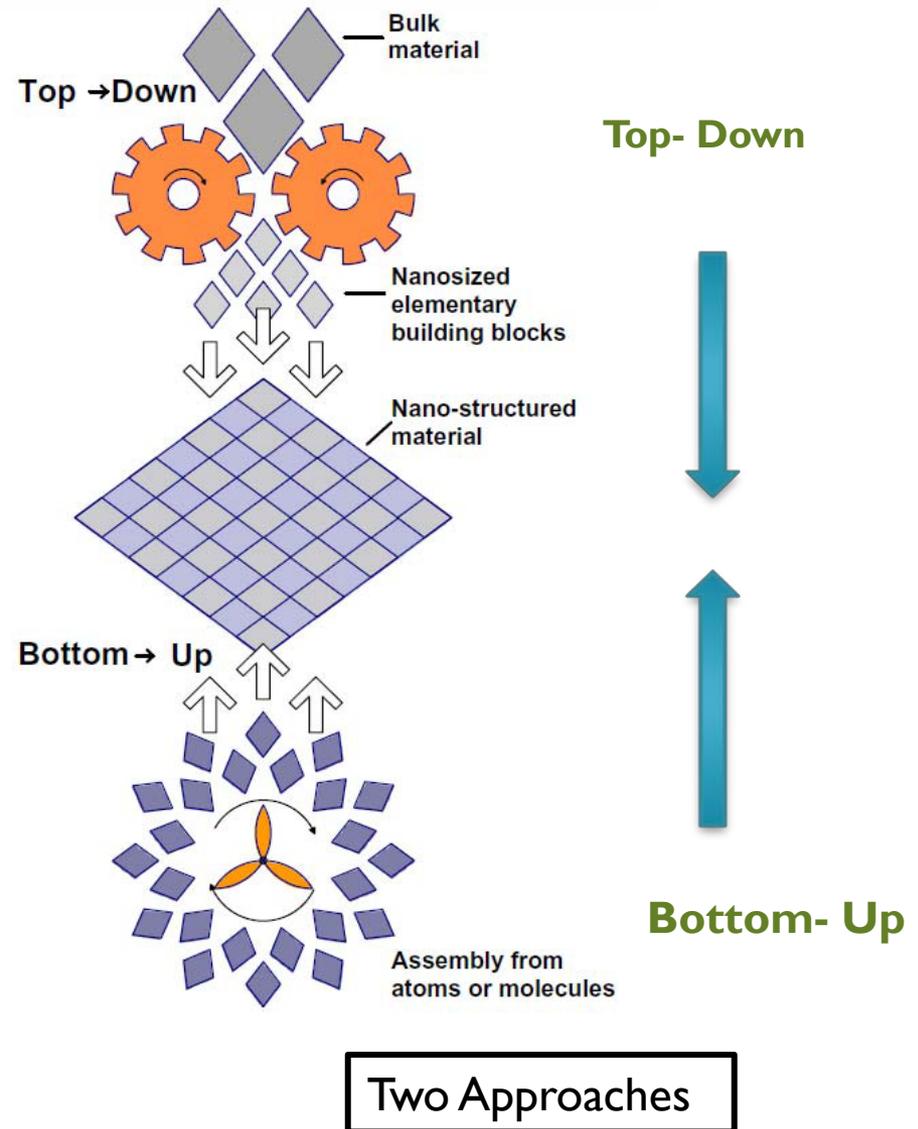
Thank You



Nanotechnology encompasses nanoscale science, engineering, and technology that involve imaging, measuring, modeling, and manipulating matter at nano-scale (1-100 nm).

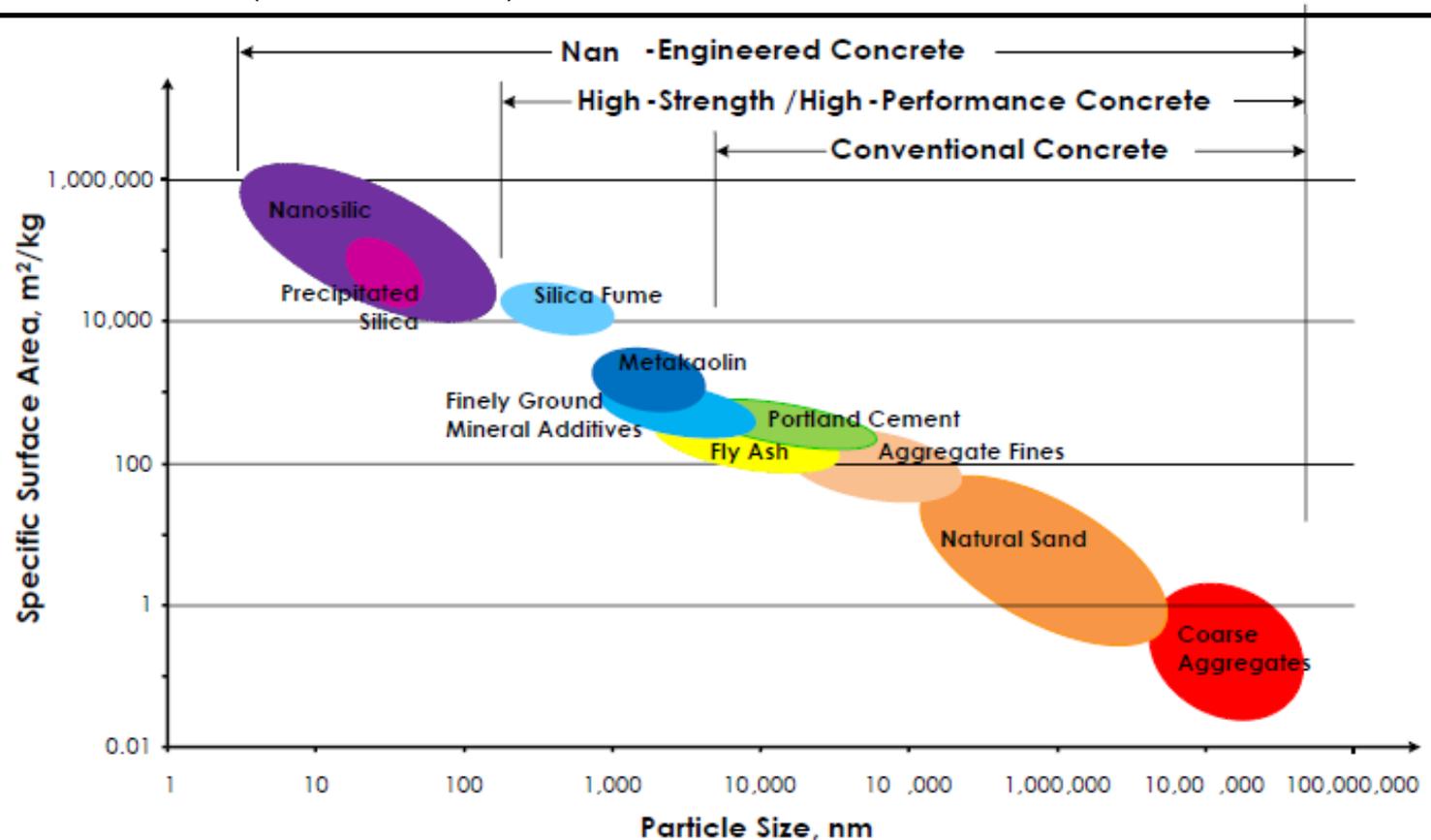
2000 Presidential Commission on Nanotechnology
(www.nano.gov)

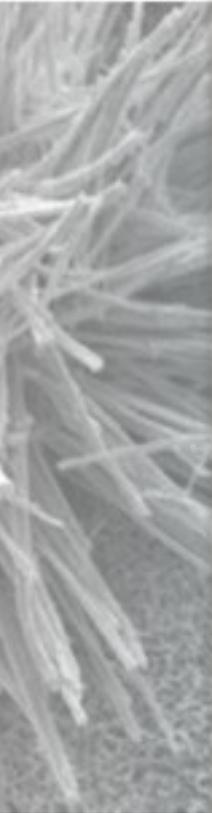
1. Economic and safe transportation –
Nanotechnology has great potential
2. Concrete-based materials are considered by the National Nano Initiative as examples where nanotechnology may have a particularly large impact in the future.
3. Engineer concrete through nanoscale optimization to significantly improve mechanical performance, durability and sustainability



Concrete: Nanostructured, Multiphase, Composite

- ❖ Amorphous phase, nanometer- to micrometer-size crystals, and bound water along with aggregates
 - ❖ Mechanical properties – structural elements and phenomena in micro- and nanoscale
 - ❖ C-S-H size lies in the few nanometers range
 - ❖ C-S-H structures – layers of solids separated by gel pores, filled with interlayered and absorbed water, sensitive to moisture movement (shrinkage, cracking)
- ❖ Degradation mechanisms – multiple length scales (nano to micro to macro), properties of each scale derive from those of the next smaller scale
- ❖ Nano-engineering of concrete – solid phases, liquid phases, interfaces between liquid-solid, and solid-solid (Garboczi, 2009)





Key Breakthroughs in Concrete Technology Through the use of Nanotechnology (Birgisson et.al., 2010)

- ❖ Development of **high-performance cement and concrete** materials - superior mechanical and durability properties
- ❖ Development of **sustainable concrete materials and structures** through engineering for different adverse environments
 - ❖ Reducing energy consumption during cement production and enhancing safety
- ❖ Development of **intelligent concrete materials** through the integration of nanotechnology-based **self-sensing, self-cleaning, self-healing** and **self-powered** materials
- ❖ Development of **novel concrete materials** through nanotechnology-based innovative processing of cement and cement paste
- ❖ Development of fundamental **multiscale model(s)** for concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macroscales.

Areas of Improvement in Concrete Properties



- **Strength**

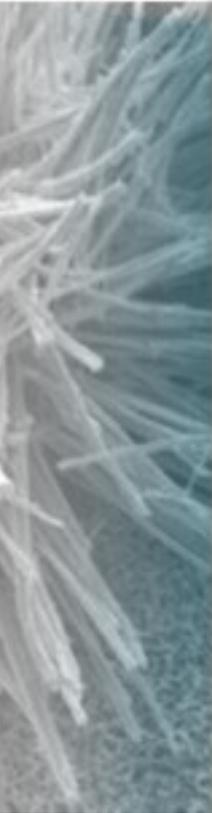
- **Conductivity**

- **Durability**

- **Self-healing**

- **Ductility**

- **Self-cleaning**



Nanomaterials used in concrete:

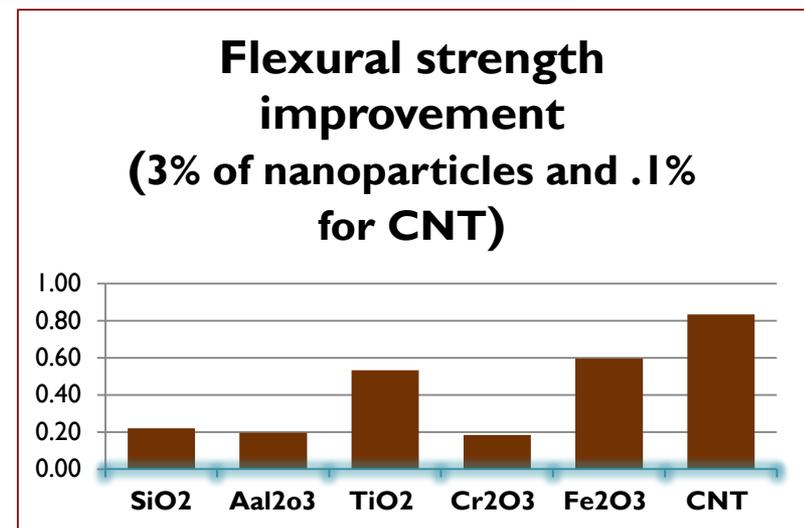
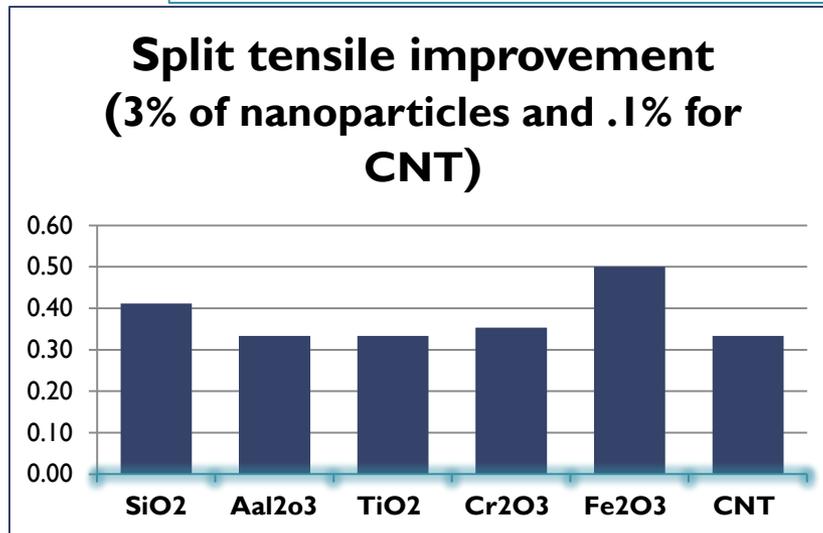
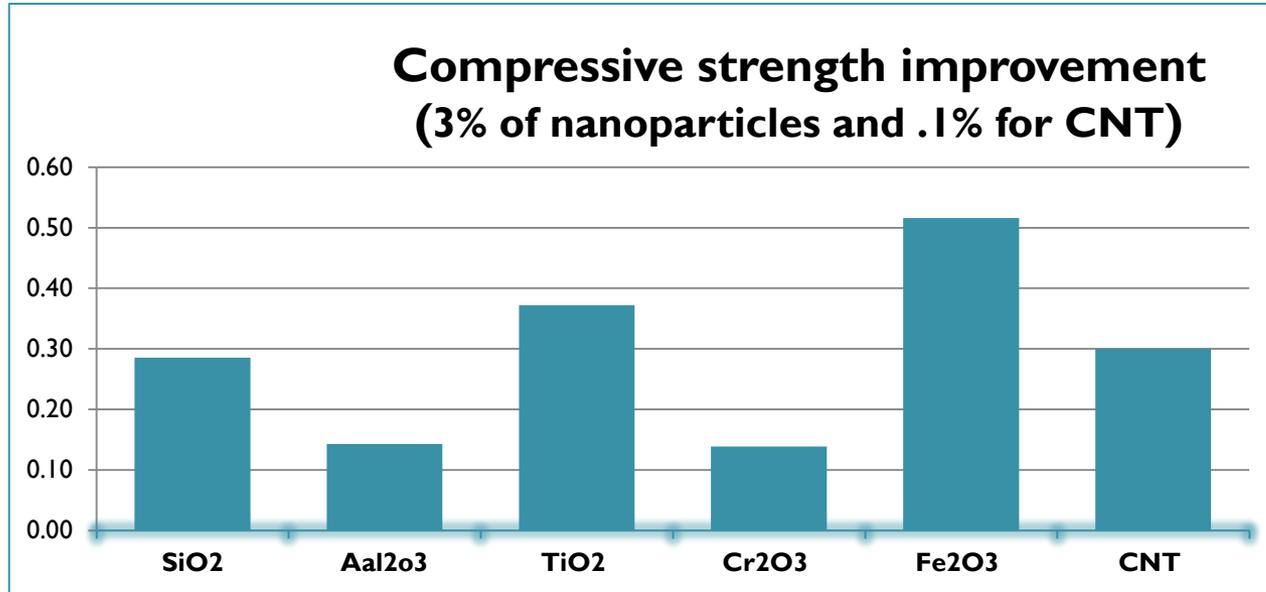
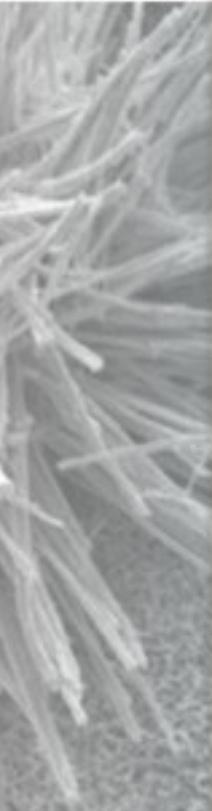
- Nano-SiO₂
- Nano-Fe₂O₃
- Nano-Al₂O₃
- Nano-TiO₂
- Nano-Cr₂O₃
- Nano-CaCO₃
- Nano Clay
- Carbon nanotubes/nanofibers (CNTs/CNFs)
- (Li et al., 2004; L. Hui, 2004, Sobolev et al., 2009, Ozyildirim and Zegetosky 2010)

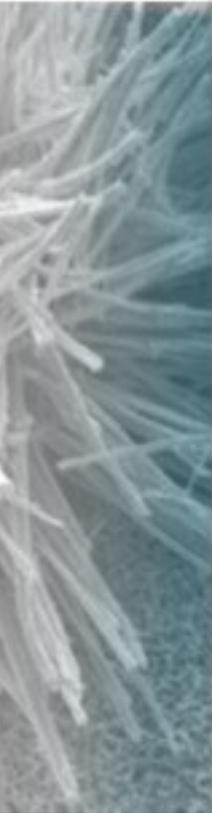
Mixing and Dispersion

	CNFs / CNTs	Nano-SiO ₂	Colloidal-SiO ₂
Dispersion	Mix CNFs with deionize water-superplasticizer* solution and disperse using a sonicator at an amplitude of 30% for 15 minutes.	Mix nanosilica powder with deionize water and disperse using a ultrasound at an amplitude of 50% for 5 minutes.	Water-based nanomaterials (no need of sonication)
Mixing procedure	<ol style="list-style-type: none">1. Mix cement + fine aggregate2. Add coarse aggregate and mix3. Add (water + dispersed nanomaterials) and mix		<ol style="list-style-type: none">1. Mix cement + fine aggregate2. Add coarse aggregate and mix3. Add 95% water and mix4. Add high range water reducer (polycarboxylate) and mix5. Add colloidal nanosilica and mix6. Add the remaining 5% water and mix

* Use of polycarboxylate-based HRWR proved successful in disaggregating the CNFs in solution and improved the dispersion of CNFs in the cement paste

Mechanical properties: Compressive, Split tensile & Flexural Strength





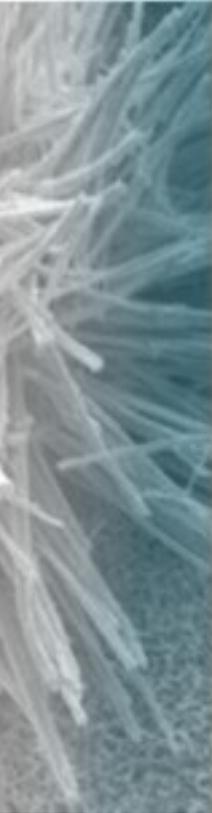
Modulus of elasticity and Toughness

MOE

- **Nano Al₂O₃ was found to be very effective in increasing the MOE of cement mortar (Zhenhua et al., 2006)**
 - **5% addition of nano-Al₂O₃ (150 nm Avg. size) causes 143% increase of MOE at 28 days**
 - **Increase of compressive strength was not very obvious**
- **At higher replacement level (e.g., >5%), agglomeration of nanoparticles caused ineffective densification of ITZ and as a result, the elastic modulus of mortars decreases.**

Toughness

- ❖ **The reinforcement of combined nanocellulose and microcellulose fibers in **reactive powder concrete (RPC)** was found to be effective in increasing the toughness of an otherwise brittle material.**
 - ❖ **3% micro- and nanofibers - the fracture energy by more than 50% relative to the unreinforced material (Peters et al., 2010).**



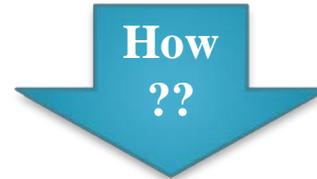
Nanoporous Thin Film Technology (NPTF)

- Water suspended small quantity of nanoparticles (**colloidal suspension**) are used to **coat aggregate** through dip- or spray coating methods
- Effective way to improve the ITZ – 8-22% reduction in ITZ porosity
- Improvements in compressive, tensile, and flexural strengths and reduction in drying shrinkage in mortar and concrete
- Increase of MOE in mortar
- The improvement in concrete performance can ameliorate in concrete pavements
 - longitudinal and transverse cracking,
 - corner breaks
 - punchouts
 - D-cracking

Durability properties:

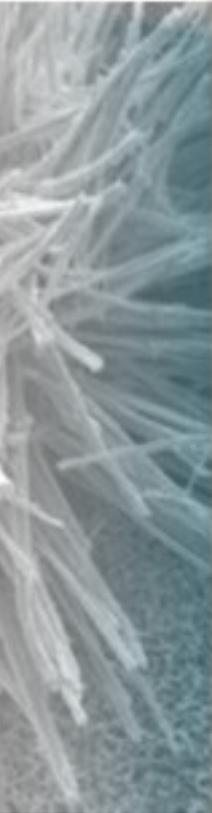
- *Reduced Permeability*
- *resistance to chloride penetration*
- *Improved Shrinkage Properties*
- *Alkali–aggregate reactions mitigation*

- Decrease in water penetration depth, gas permeability, and diffusion depth (up to **100%** or even more)!!
- Coefficients of permeability (**1-3 order of magnitude**)!!

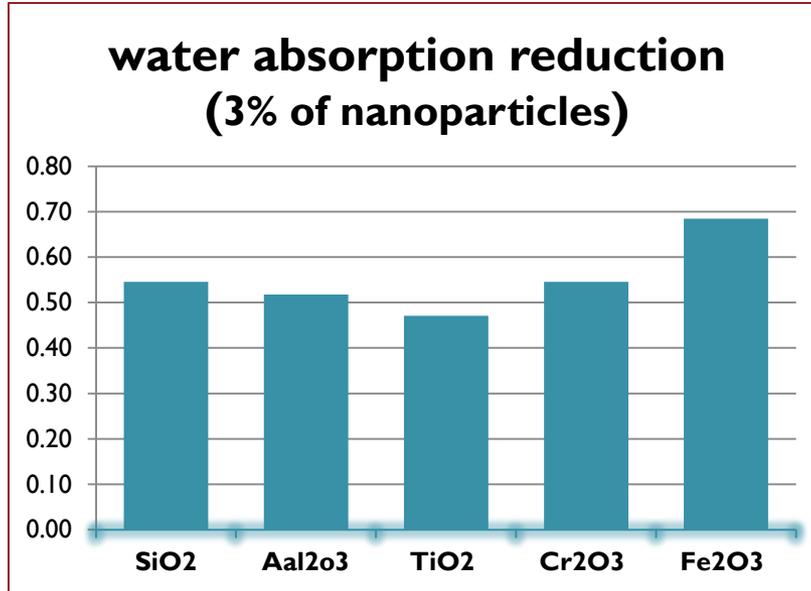


- **Formation of denser microstructure and significant improvement in ITZ**
 - Nano-particles act as nucleation site – increase in hydration rate
 - Pozzolanic reaction between nano-particles and CH
 - Improving the micro / nano-filling effects and reduction in porosity
- **Improvement in C-S-H gel**
 - Increase of avg. chain length of **C-S-H**
 - **Formation of high stiffness C-S-H – 38% and 50% for samples with 6% and 18% nanosilica, high stiffness C-S-H is more resistant to calcium leaching**

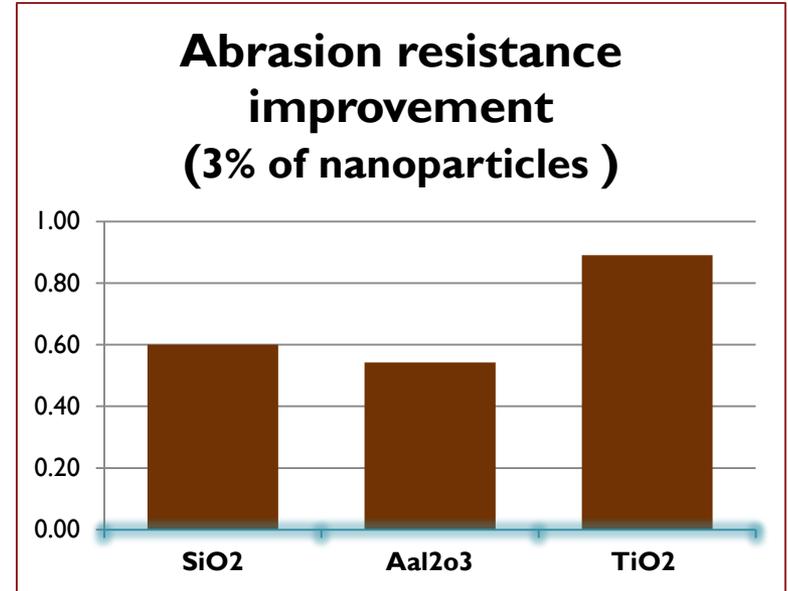
(Wagner et al. 1994, Tao Ji 2005, Mandal et al. 2010, Gaitero et al. 2008)



Water absorption



Abrasion resistance



Permeability

**Nano-
MMT**

**0.4-0.6 %
addition**

**Nano-Clay,
Nano-ZrO₂,
Nano CaCO₃**

**2-3%
addition**

**About 50%
less permeability
, more chloride
resistance**

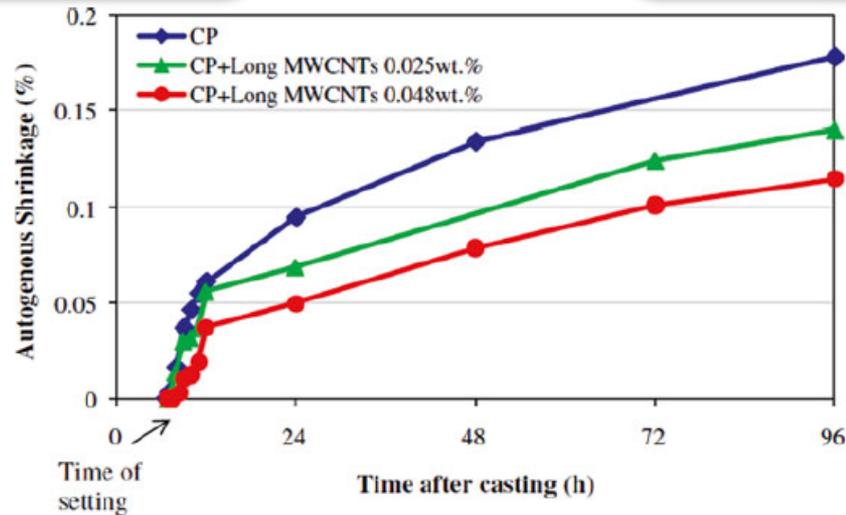
Shrinkage:

Carbon Nano-
tube (CNT):
0.048%

Nano silica:
4.5%

Autogenous
Shrinkage:
25 % reduction

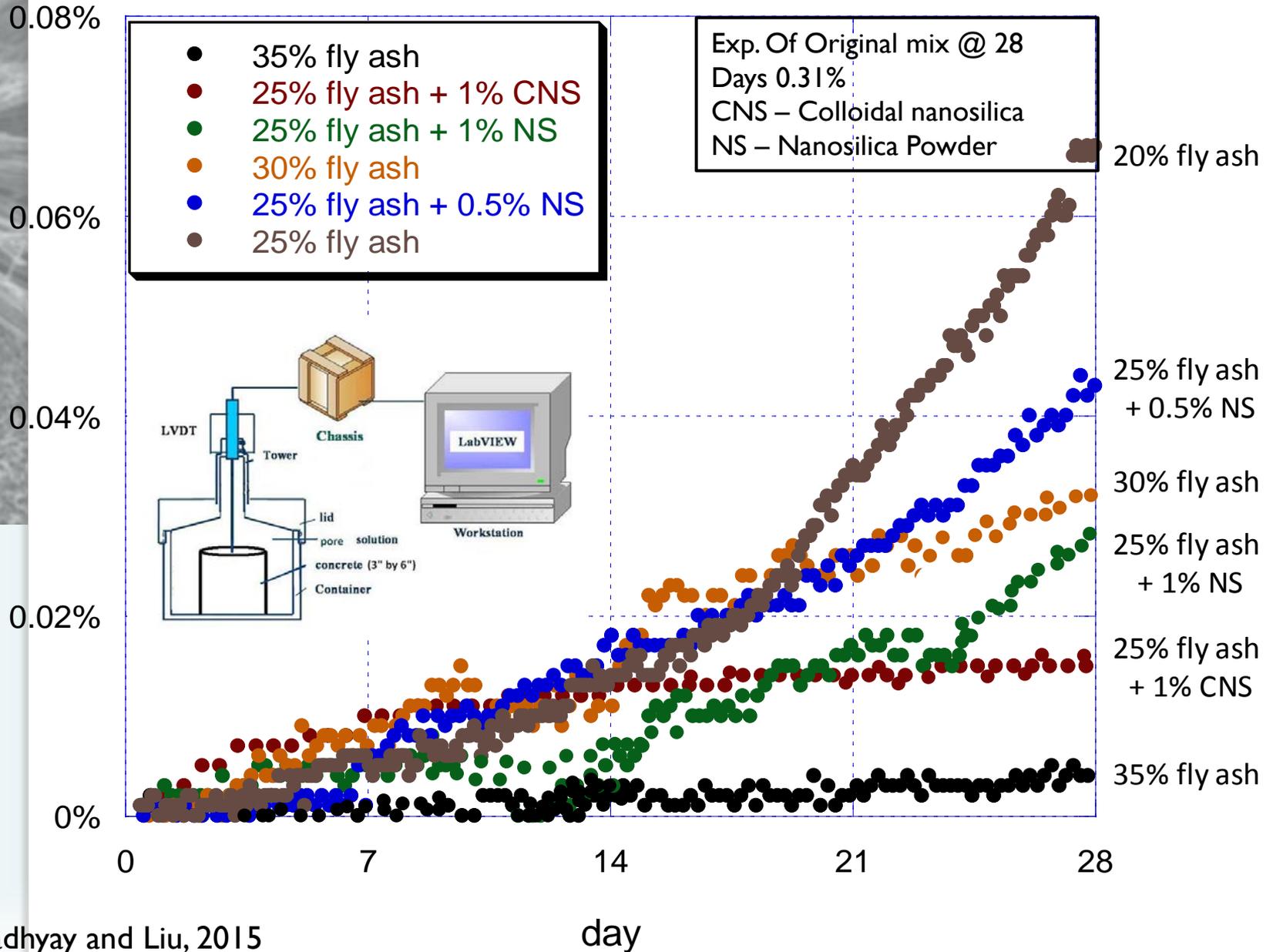
Chemical
shrinkage:
50% reduction



- Nano-clay particles shown promise (Chang et al. 2007, Kuo et al., 2006, Morsy et al. 2009, He and Shi 2008)
- (li Geng et al. 2005, Makar, 2005; G. Li et al., 2005)
- (Surendra P. Shah , Pengkun Hou , and Xin Cheng) (Jon S. Belkowitz et al.)

Effectiveness of Nanosilica along with Fly Ash to Control ASR

ACCT expansion

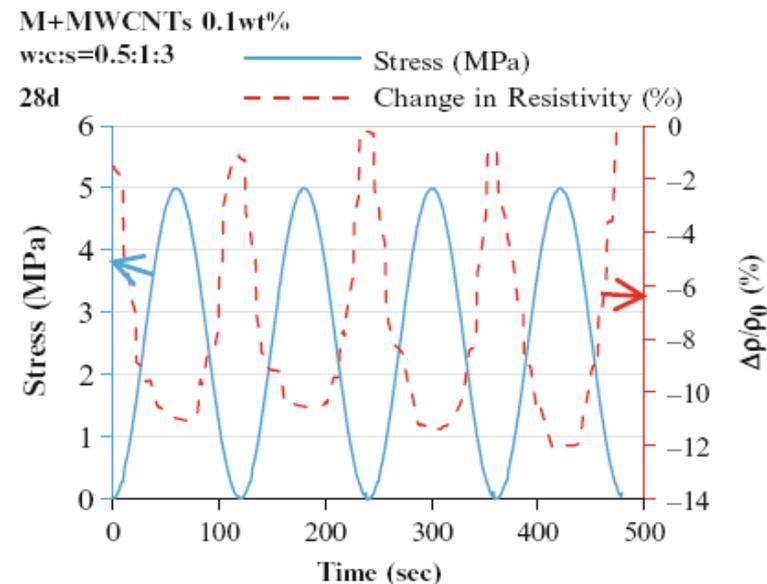


Electrical Conductivity and Stress-Sensing

- **CNTs** are the best nano materials for this purpose
- **CNTs** and **CNFs** are attached to the cement particles:
- **Cement-hybrid material (CHM)**
- Electrical conductivity: even by **40 times!!**
- (Compressive strength: by **2 times**)

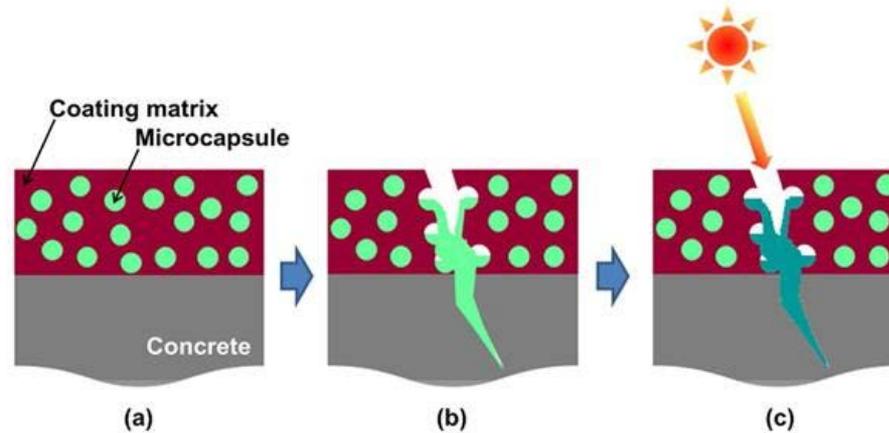
- **Self- sensing: behavior change due to stress**
- **nano-Fe₂O₃ (5%)** : self-diagnostic ability of stress
- **anatase TiO₂ (3%)**: pressure-sensitivity property
- **CNT** : Piezoresistive behavior as shown in figure

- (Li Geng et al. 2007, Nasibulina et al., 2010, Li et al., 2004)



Self-Healing of Microcracks

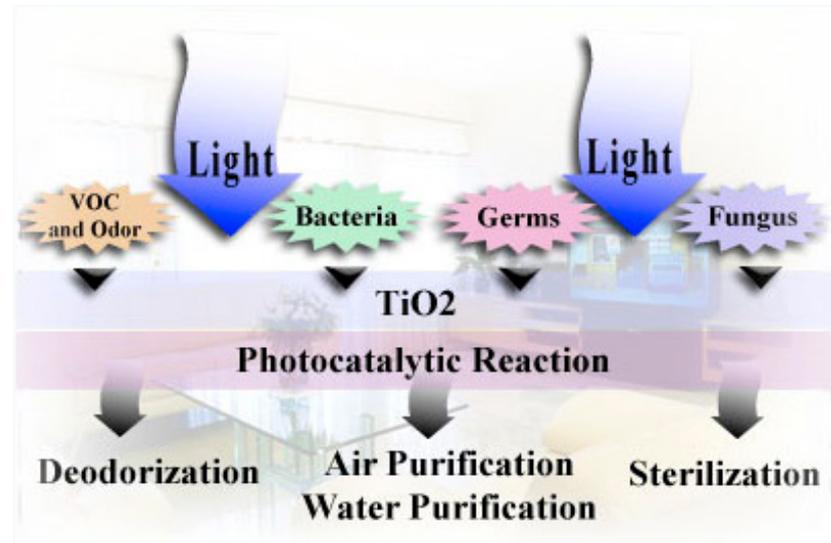
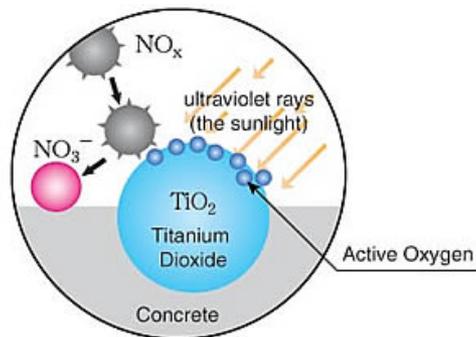
How microcapsules heal concrete cracks



Type of self-healing	Effectiveness / test	Mechanisms	Researchers
A combination of silica microcapsules containing an epoxy sealing compound and nanosilica particles functionalized with amine groups	Cylindrical concrete (4x1 inch) specimens subjected to 150 cycles of a freeze-thaw test (4 cycles per day between -20 and +20 °C)	Breaking down of the capsules during crack formation and sealing the crack	Guerrero et.al. 2015
Microencapsulated healing agent and a catalytic chemical trigger	Could be especially applicable to fix the microcracking in bridge piers and columns	Breaking microcapsules during crack formation release of healing agent and catalyst, polymerization, crack sealing	Kuennen 2004
microcapsules (PSMs) with oil core and silica gel shell	Microcapsules were dispersed in fresh cement mortar along with carbon nanofibers and silica fume. Heal at least part of the artificially induced microcracks		Yang et al., 2010

Self-Cleaning Concrete

- **TiO₂** nanoparticles:
trigger a photocatalytic degradation of **pollutants**



Photocatalytic **concrete pavement blocks** were found to be very effective in removing NO_x through **photocatalytic reaction of nano TiO₂**

Sustainable Concrete Materials

Sustainable Cements:

- **Belite cement** :Environment friendly, energy-efficient, superior durability but low early strength !!
- Adding suitable nanoparticles with optimum dosage can improve early strength

Increase of Early Strength in High volume fly ash (HVFA) concrete (50%)

- Better durability and long-term mechanical properties but low early-age strength
- The composite addition of nanosilica, fly ash, and silica fume was found to be economic and effective to achieve required early strength (Feng et al., 2004).

Nonconventional Aggregates in concrete with the aid of nano modification

- ❖ Incinerator bottom ash
- ❖ Modified by colloidal nano silica (3 wt%)
- ❖ Approximately 60% increase in compressive strength

Geopolymers concrete: waste management

- ❖ Properties enhancement through nanoparticles (5-10%)
- ❖ Up to 40% compressive strength increase

Field application:

- Mostly:

Nano-SiO₂

Nano-TiO₂

- Field project by the U.S. Army: nanosilica in a grout
- To reduce the urban heat island effect : high-performance cementitious coating (HPCC) !!



Two successful examples!

Parking area in the heart of Phoenix: **3 years data** of good performance!!



Use of *photocatalytic concrete face mixture* in precast wall panels of Louisiana State University 4 Pete Maravich Assembly Center.

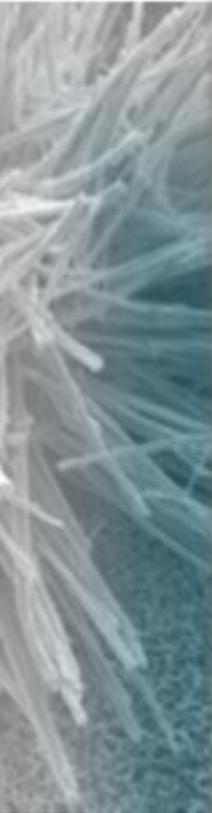


Other Applications

- ❖ Nanosilica was used to improve segregation resistance for **Self consolidated concrete** (SCC)
- ❖ In a project near Venice, Italy : nano-SiO₂ in SCC
- ❖ Use of nanoclays for producing SCC for slip form paving
 - ❖ National Pavement Technology Center at Iowa State - addition of a nanoclay in very small dosages (1%) and Class C fly ash was effective to maintain a balance between flowability during compaction and stability after compaction without the need of internal vibration.
- ❖ Application of nano-engineering to develop environment friendly and multifunctional materials (mixes) for repair and thin overlay applications
- ❖ Evaluate and demonstrate the feasibility of self-powered pavement deicing and self-sensing system using of conductive paving materials – both Portland cement concrete and asphalt concrete.

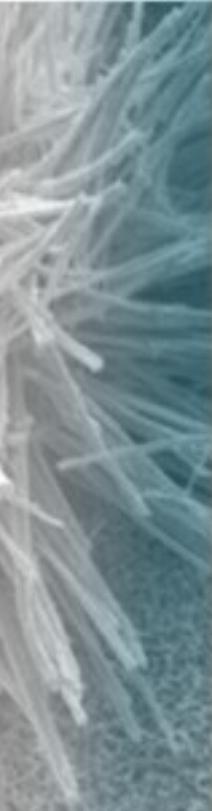
Challenges:

- Energy- effectiveness
 - Cost- effectiveness
- solution** → Chemical production
Mass production
- Slow adoption rates of new technologies and Funding
- Needs Industry's Attention!!
- Imaging equipment
- solution** → Technology progress
-



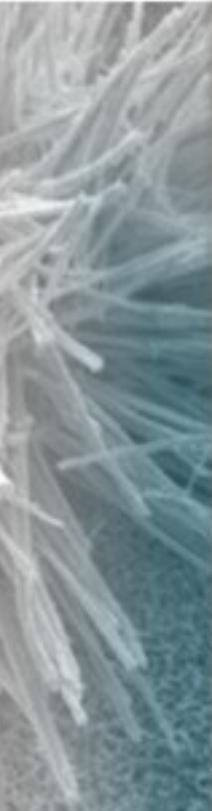
Applications of Nanotechnology in Transportation

Dr. Xiong (Bill) Yu
Case Western Reserve University



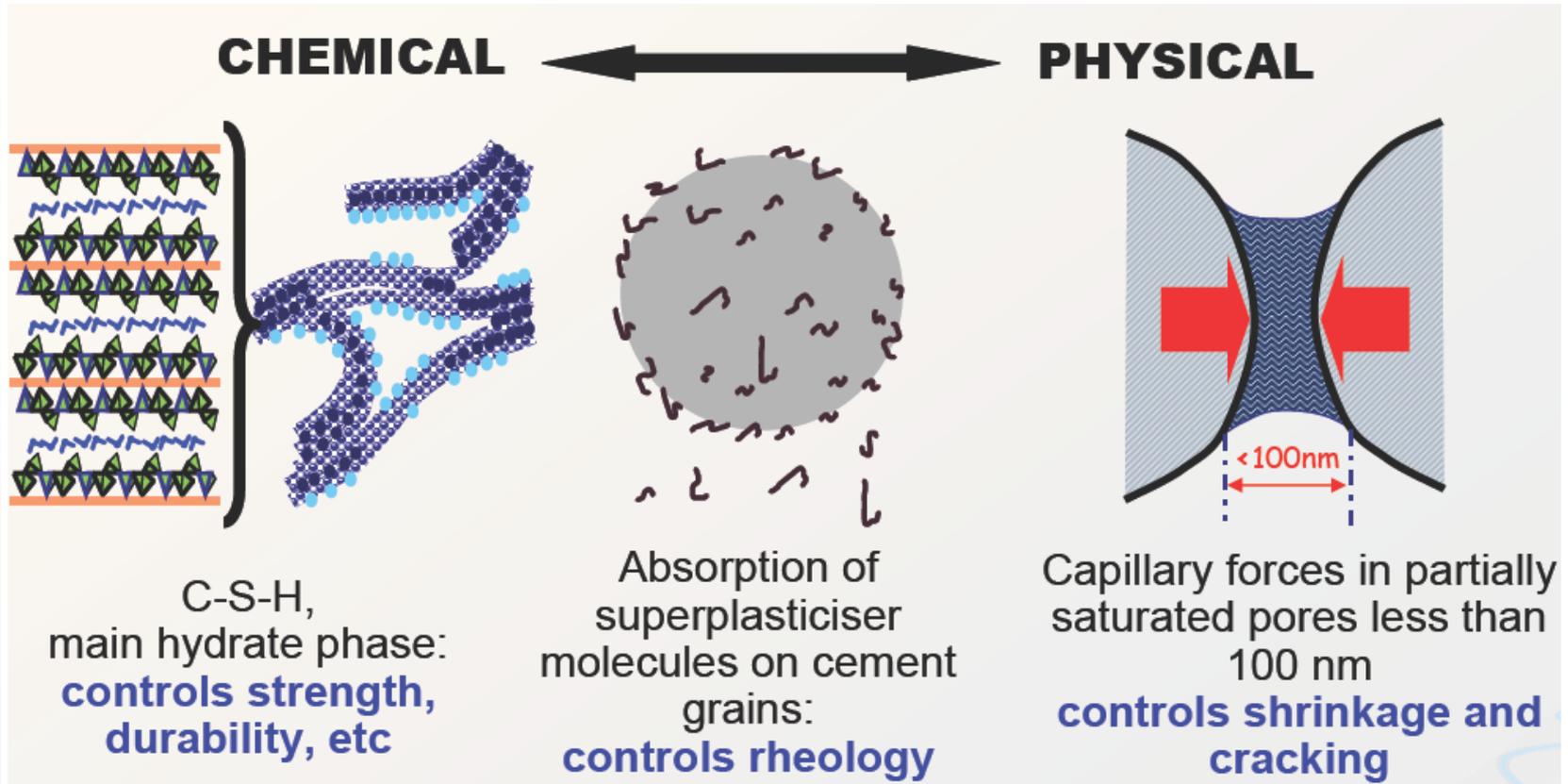
Applications of Nanotechnology in Transportation

- New toolsets to understand the fundamental mechanism for infrastructure performance and deterioration
 - Hydration, HD LD CSH gel
 - ASR gel, ...
- Engineering high performance materials
 - Improving performance
 - Beneficial use of waste
 - Multi-functionalization

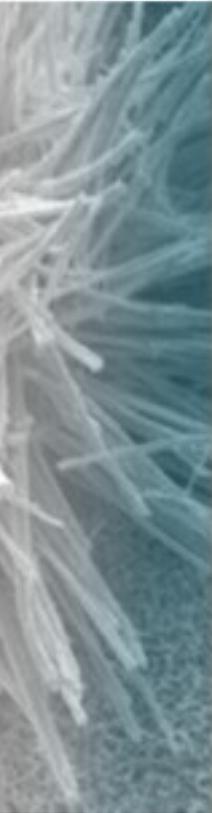


New nanoscale tools to understand fundamental mechanism

Nanostructures Determining Concrete Performance



Partl et al. 2006

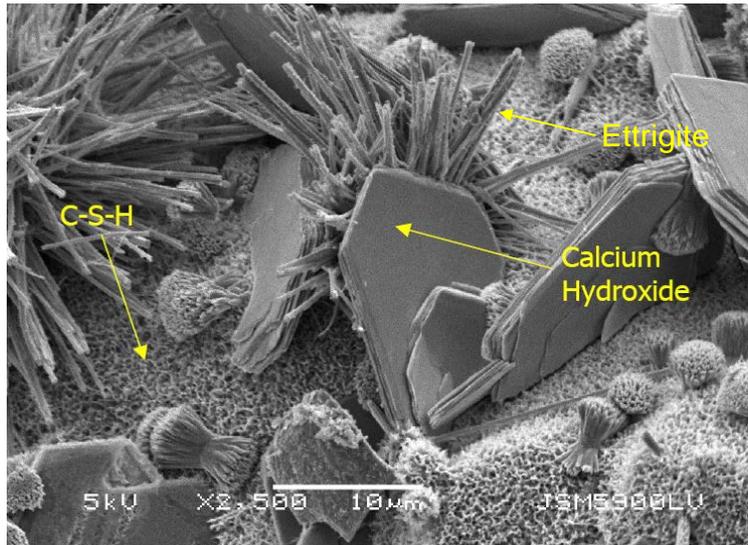


Methods to Probe the Nanostructure of Cement

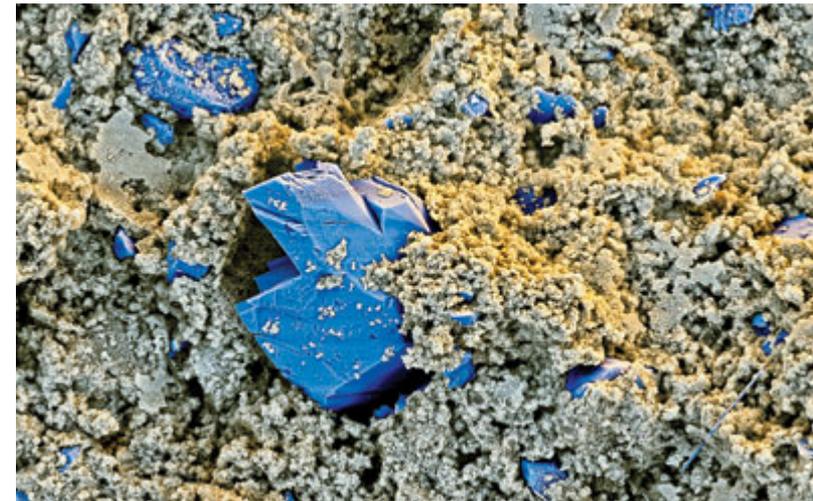
- Experimental tools
 - Atomic Force Microscope (AFM)
 - Small Angle Neutron Scattering (SANS)
 - Small Angle X-ray Scattering (SAXS)
 - Transmission Electron Microscopy (TEM)
 - Scan Electron Microscopy (SEM)
 - Nanoindentation
 - Nuclear Magnetic Resonance (NMR)
 - ...

Structures in hydrated cement paste

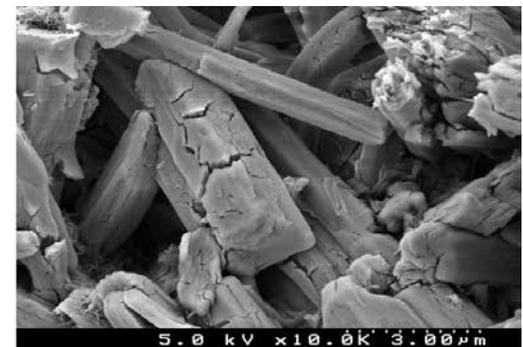
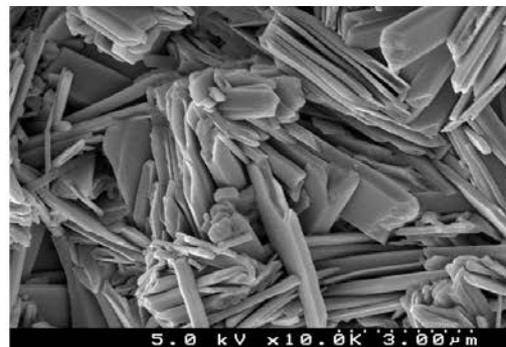
- Microstructure and crystalline structure



Modified from Garboczi and Bentz 1995



concrete (brown) crystallizing around X-Seed crystals (blue)

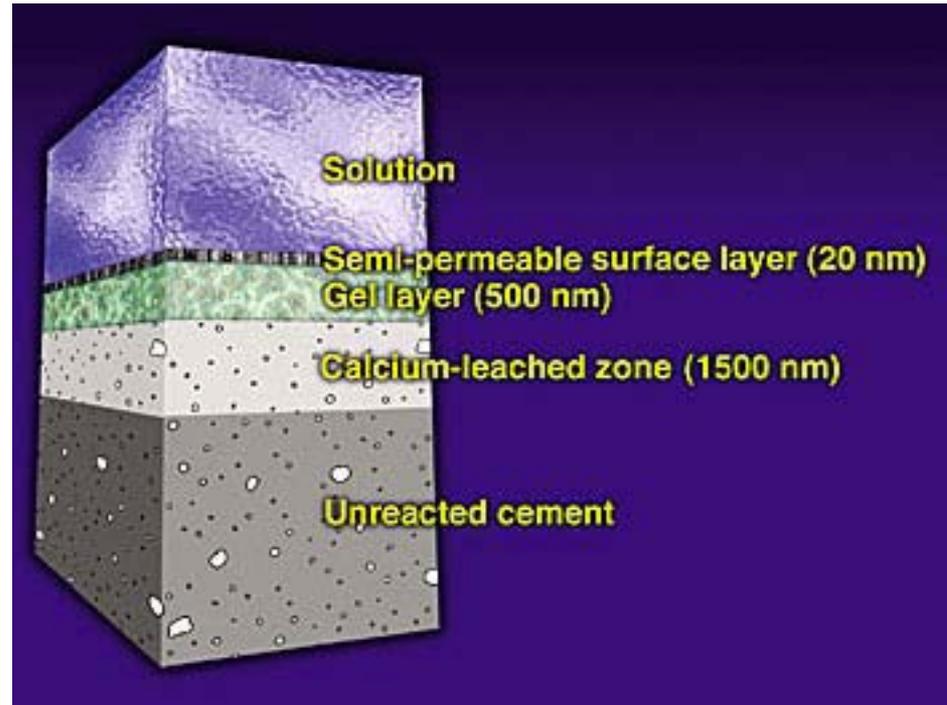


Change of crystalline microstructure with nanoparticles (Zhang and Yu 2012)

I. Cement Reactivity at Nano-Scale

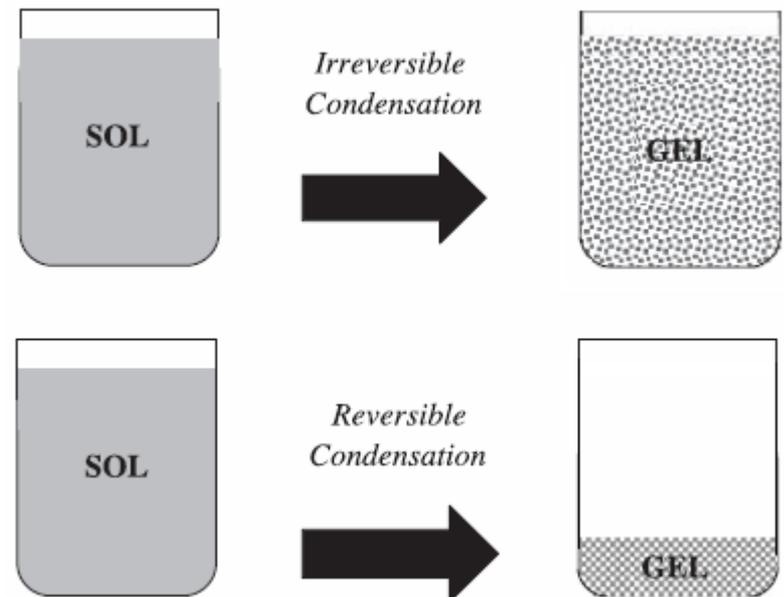
(Livingston and Schweitzer 2007; Balaguru and Chong 2007)

- Nuclear resonance reaction analysis (NRRA)
 - Track water penetration and layer formation
 - 4 active layers



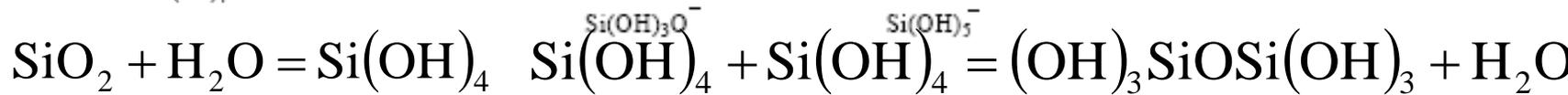
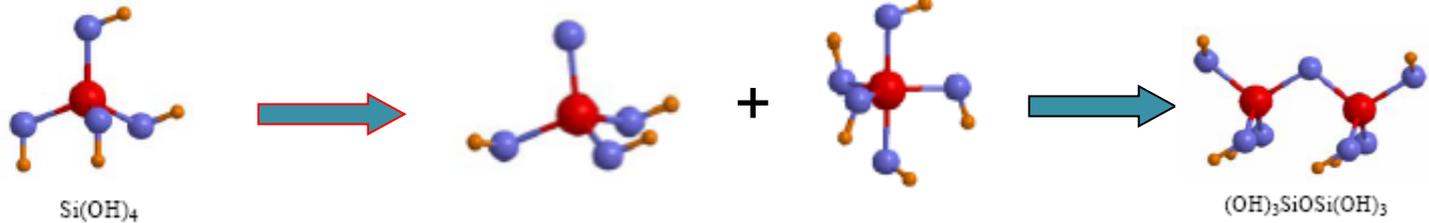
2. Kinetics of C-S-H gel formation

- Sol-gel process
 - Sol: produce solution of fine colloidal particles (mixing)
 - Gel: link colloidal particles into a continuous solid phase (setting and curing)
- Condensation: linking hydrolyzed molecules together

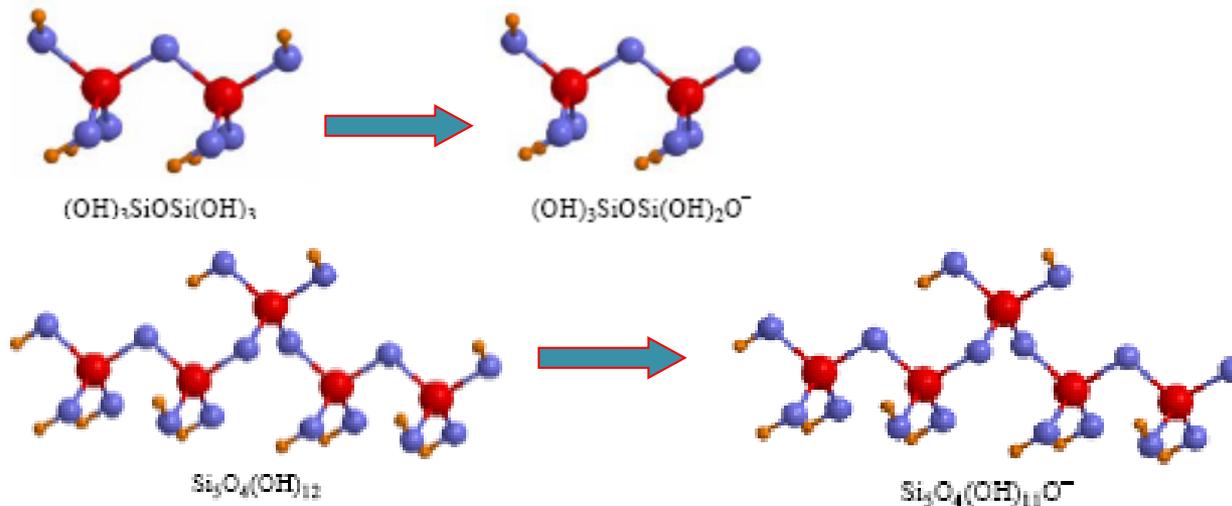
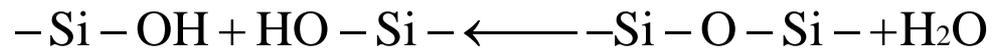


Silica Chain Formation

- Hydrolysis in basic pore environment

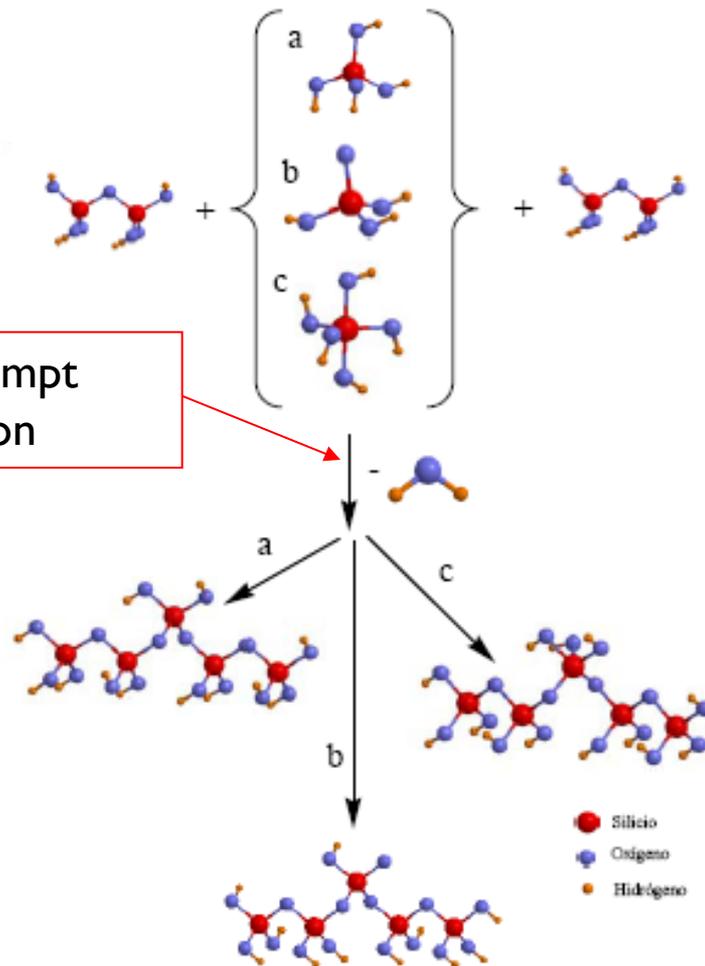


- Gel condensation into a continuous solid phase

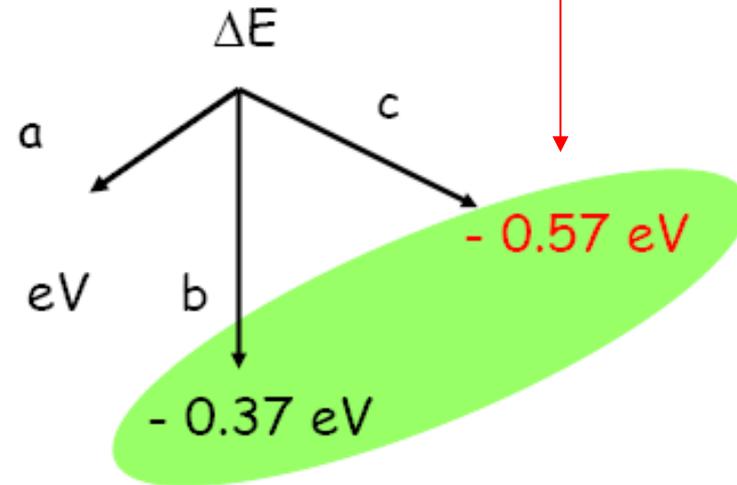


Molecular Simulations for Silica Chain Formation (Dolado 2005)

- Electrochemical potentials
- Deterministic versus probabilistic



Minimization of potential energy



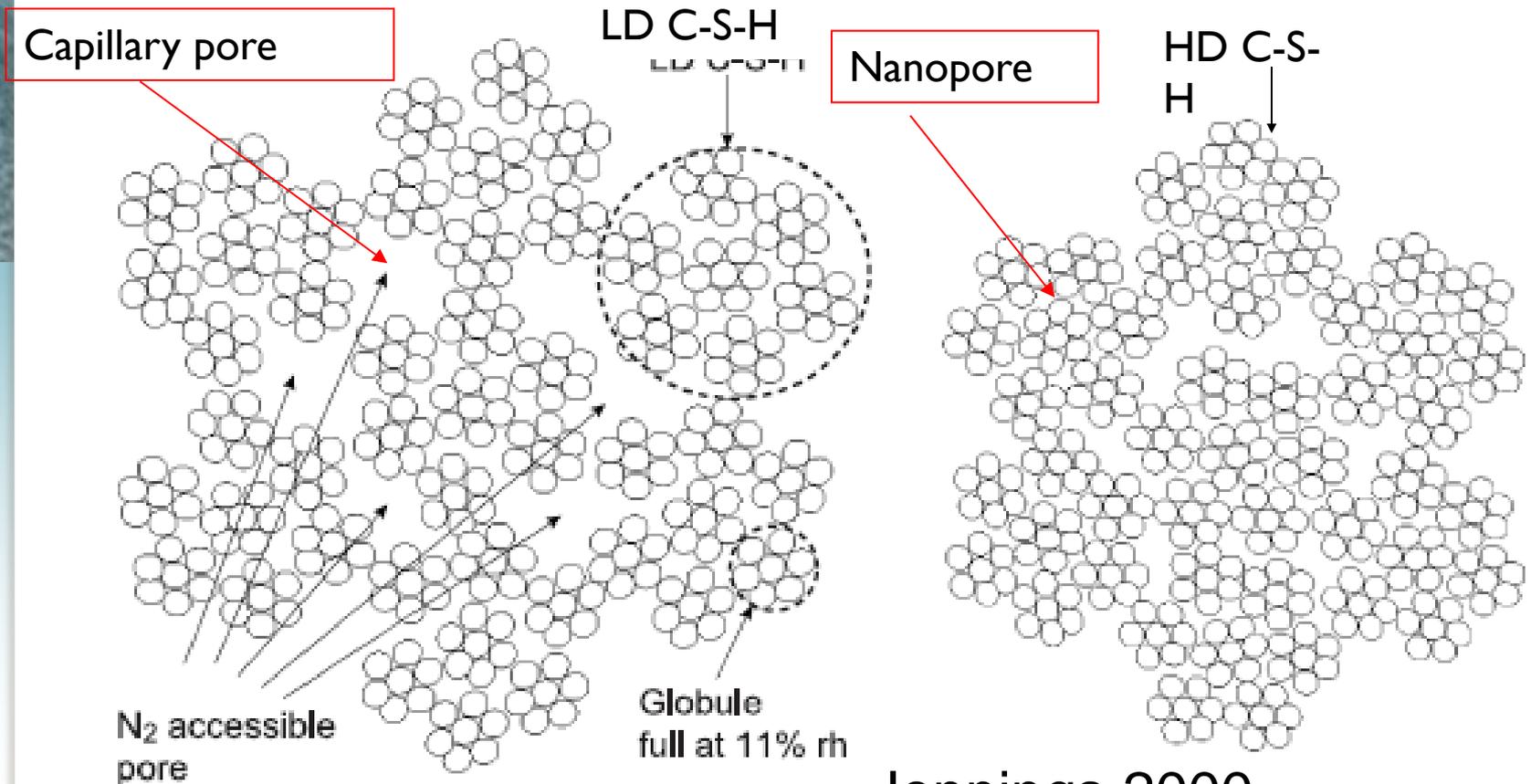
Dolado 2005

Basic solution prompt structure formation

3. Pore Spaces and Moisture Status in Cement: Creep, Dry Shrinkage, Freezing Damage

- Colloid Structure of C-S-H

- tobermorite-like or jennite-like particle -> Globules->LD and HD structure

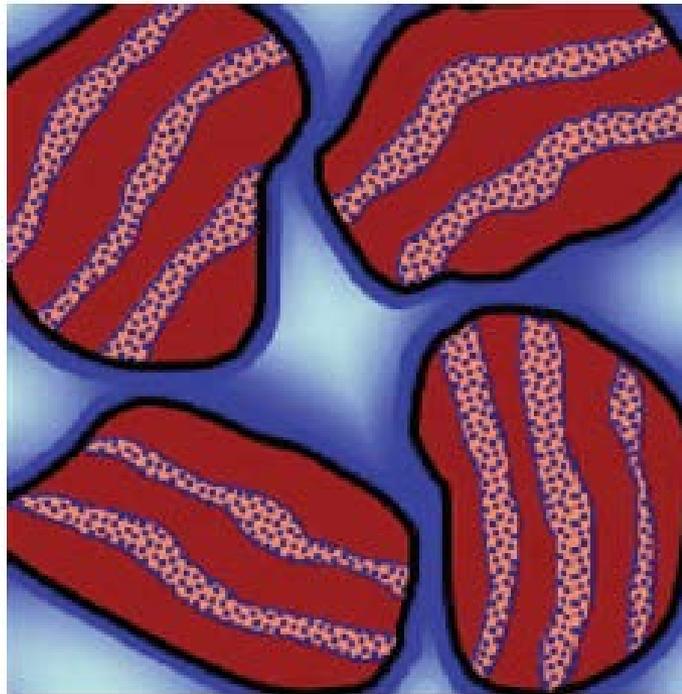


Jennings 2000

Composition and Mass Density in Nanoscale C-S-H gel (Allen et al. 2007)

- First direct measurement
 - Small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS)
 - Size scale range from nano to micrometres

• t



Calcium silicate sheets
with OH⁻ groups



Interlayer space with
physically bound H₂O



Adsorbed H₂O



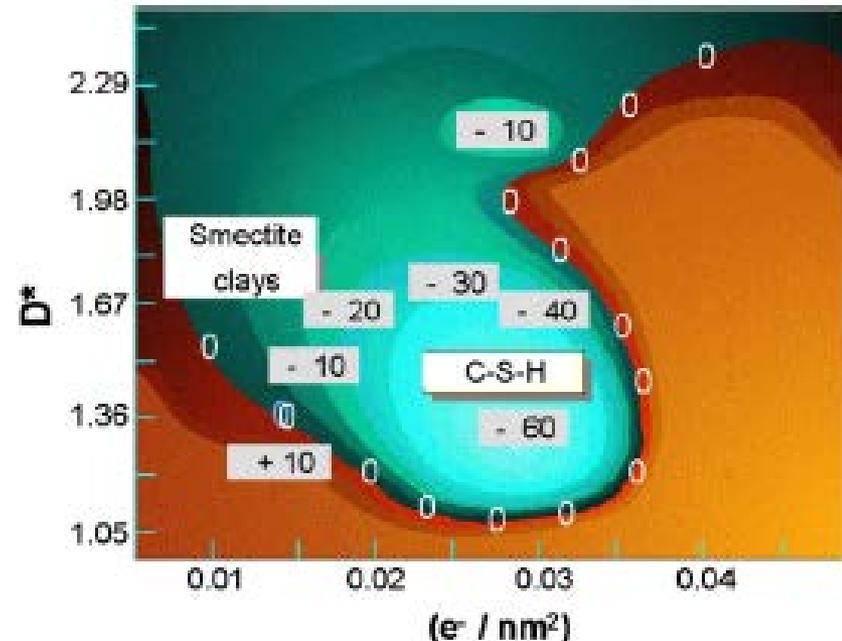
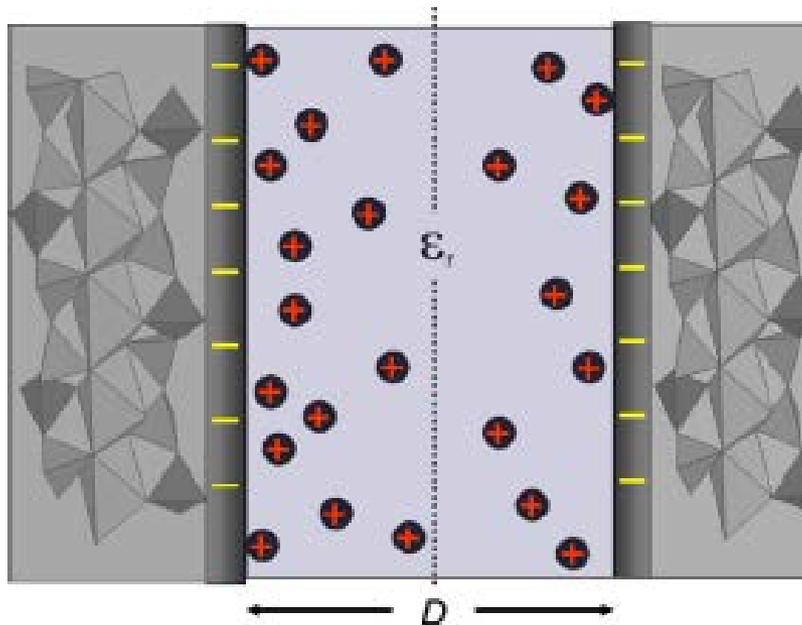
Liquid H₂O in
nanopores

density

5 nm

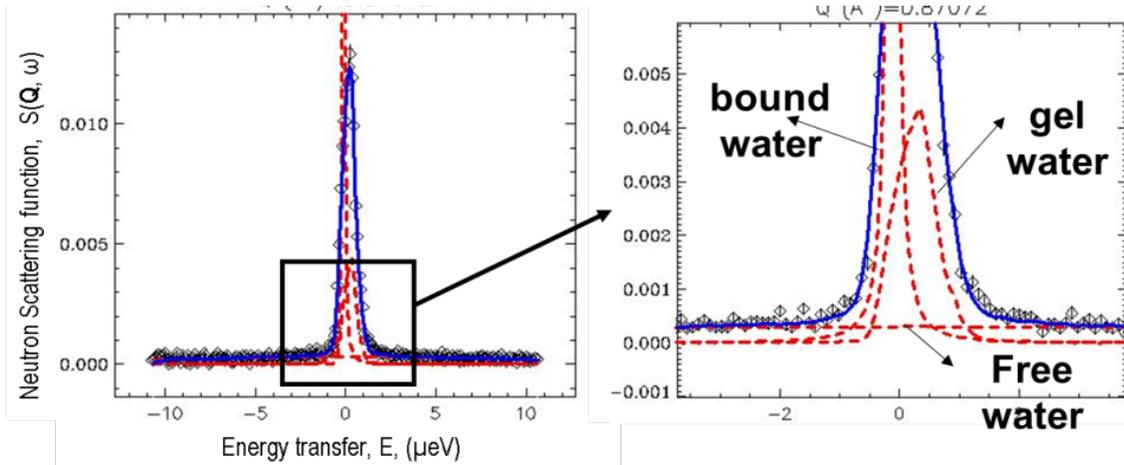
4. Engineering the Cohesion in Cement (Pelleng et al. 2007)

- Short range attractive force between C-S-H lamella via ionic correlation force.
 - strongly localized calcium ions and water molecules
 - nm- or multi-nm-thick layers of mobile water molecules and ions

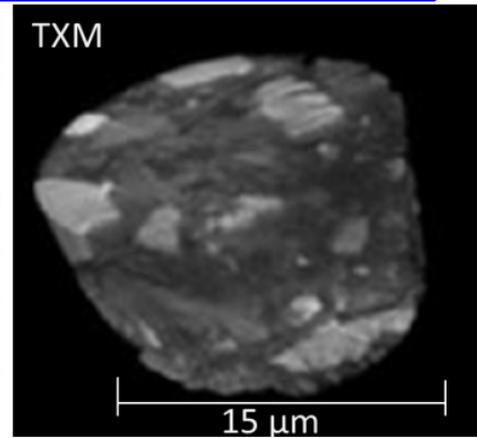
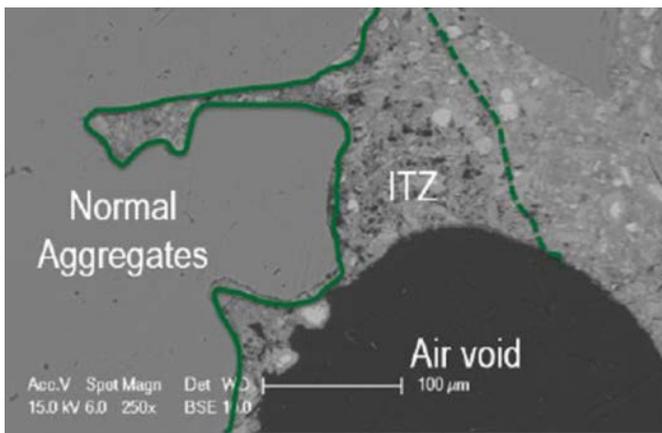


Pelleng et al. 2007

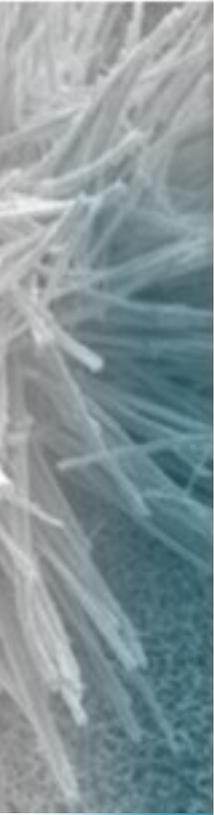
5. ASR



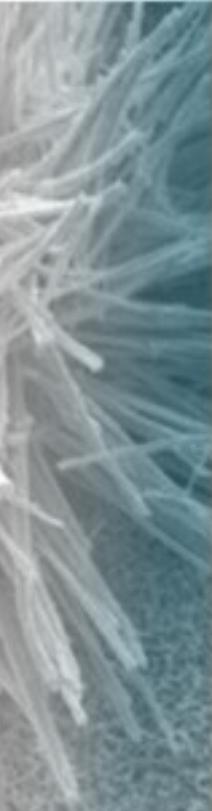
Neutron backscattering spectrometer to capture water transition at fundamental level



SEM and TXM Microstructure characterization



Engineering high performance materials

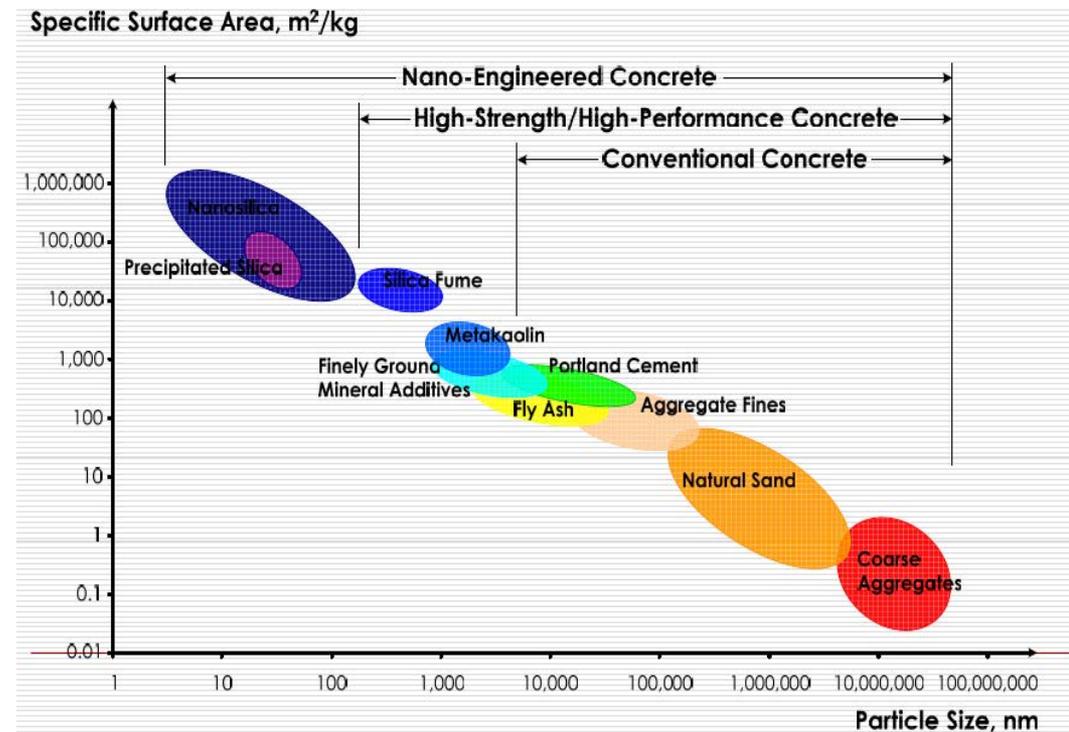


Potentials of Nanotechnology

- Lighter and stronger structural composites
- Low maintenance coating
- Improving pipe joining materials and techniques.
- Better properties of cementitious materials
- Reducing the thermal transfer rate of fire retardant and insulation materials
- Increasing the sound absorption of acoustic absorbers
- Increasing the reflectivity of glass

Nano-Engineered Concrete

- Strength, hydration, durability, weather resistance, self-healing, intelligent, environmental responsive



Sobolev and Ferrada-Gutiérrez 2005

Nanostructured Steel

- Corrosion, strength, toughness, fire resistance

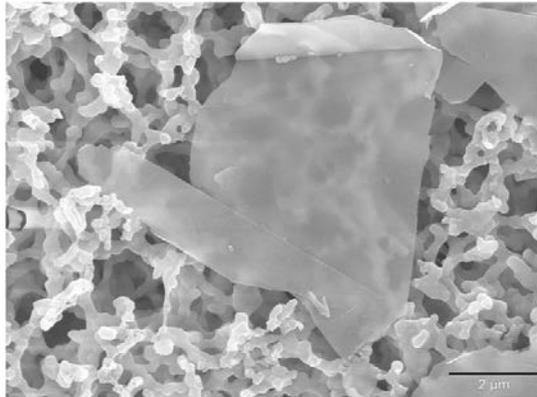


Nanostructured MMFX 2 steel rebar used in the foundation of a bridge in Tarpon Springs, Fla.

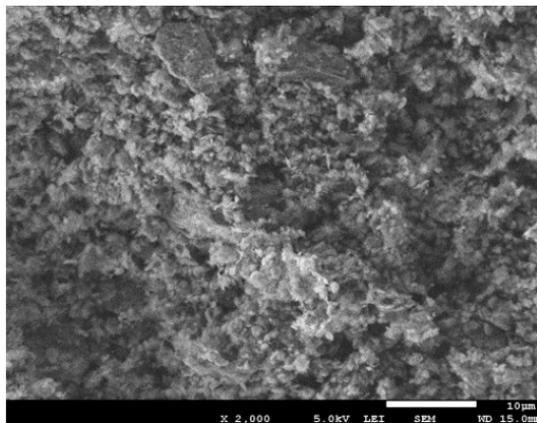
- Used in buildings, highways, and bridges and has an expected service life of 200 years.
- Twice as strong as conventional steel: requiring less steel to do the same job.
- More expensive than conventional material but with reduced labor costs.

Nano-Engineered Asphalt

- Nano-modifier, crack resistance, self healing, green asphalt, self-sensing



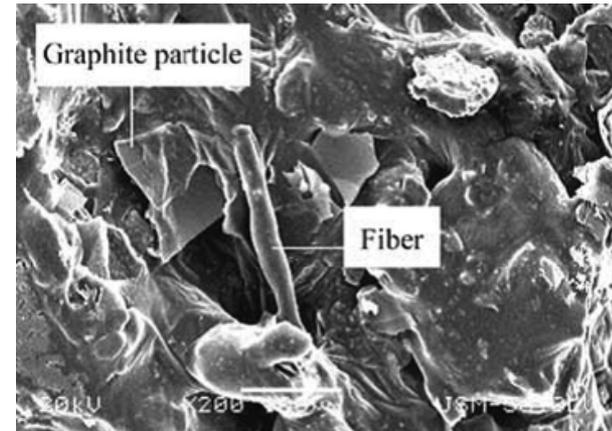
Graphene Nano-Platelet (GNP) Reinforced Asphalt (Li et al. 2015)



Conductive asphalt with ultra-high surface area graphite (Park et al. 2014)



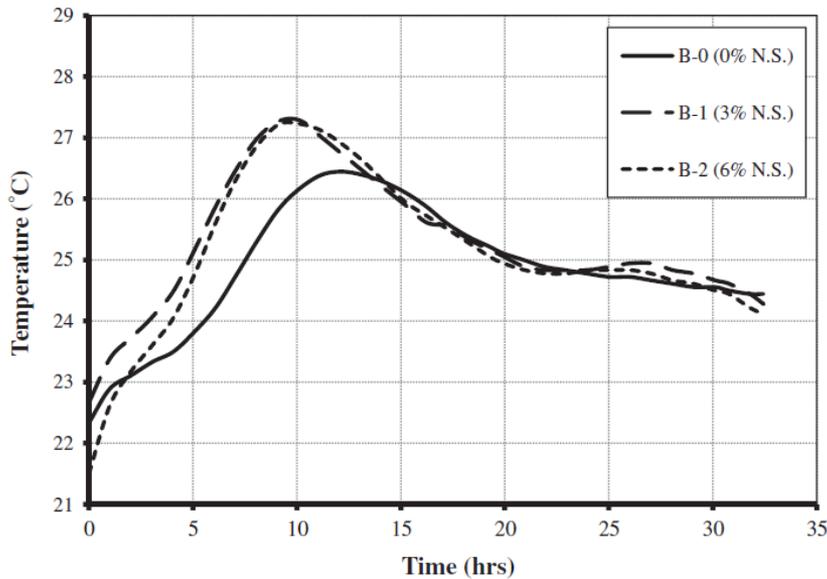
"Cool pavement" at Duffy Charter School, Phoenix AZ; Phoenix Recovery Zone



Carbon fiber asphalt for accelerated healing and ice removal (Pan et al. 2014)

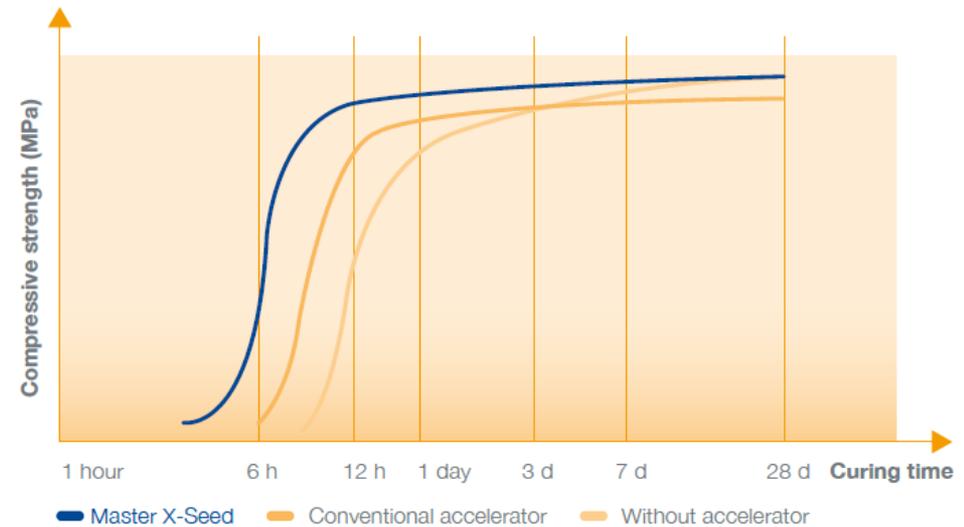
Beneficial use of waste materials

- Use of nanomaterials or fine tune the nanostructures to achieve the desirable performance.



Seeding fly-ash concrete with small amounts of nanoparticulate silica (N.S.) accelerate hydration (Said et al. 2012; Shah et al. 2014)

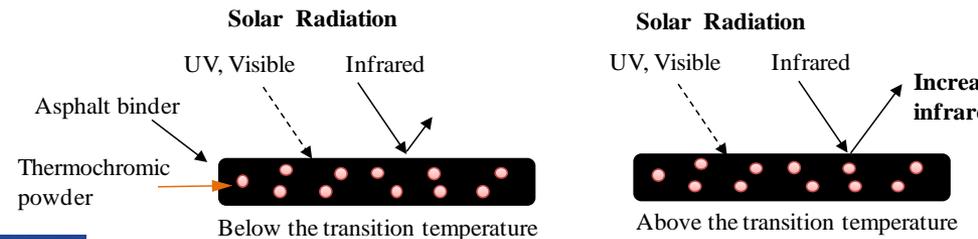
Strength Development – The Effect of the Accelerator
(380 kg/m³ CEM I 52.5 R)



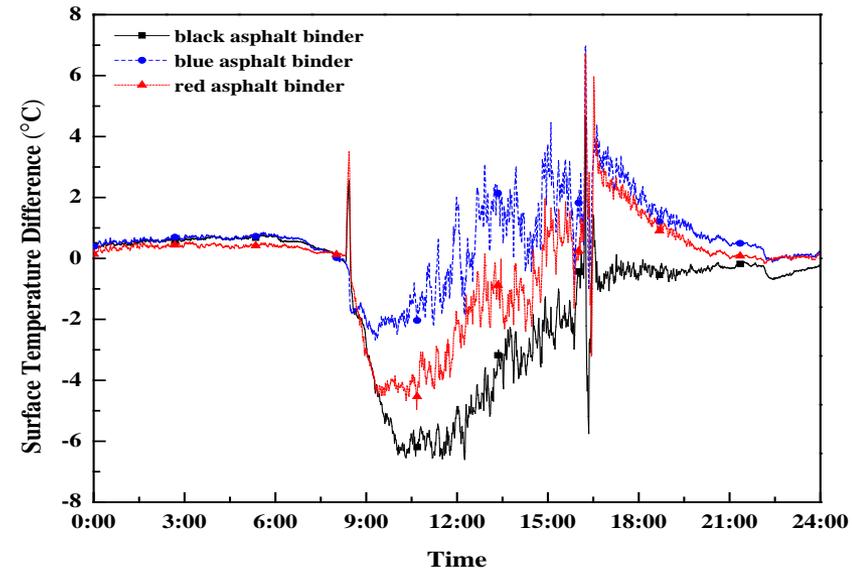
BASF X-Seed, nanocrystals of calcium silicate hydrate, creates many sites for nucleation, accelerating the speed of hydration

Multifunctional Materials

- Responsive to stimuli (thermal, chemical, mechanical, environmental, optical, biological,)



Smog-eating nanostructured substance could cut the city's air pollution in half. (Greenharmonyhome)



Thermochromic asphalt reduces pavement surface temperature (Hu and Yu 2014)