Multi-scale Performance and Durability of Carbon Nanofiber/ Cement Composites

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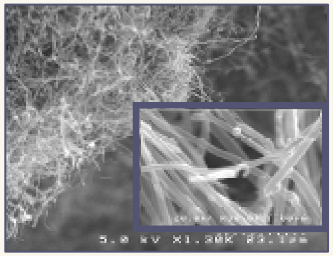
Motivation

- Increase interest in multi-functional, structural composites
  - Demand for smart structures with superior mechanical and functional properties
  - Importance of weight savings

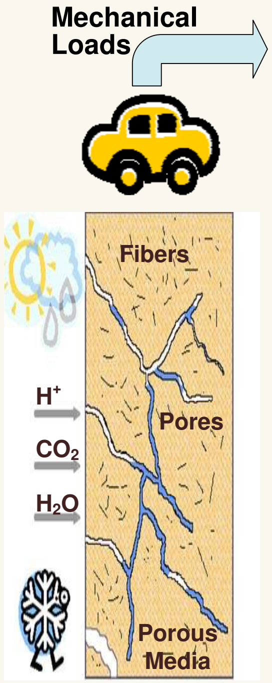


Carbon nanofibers

- Nanofiber/cement composites
  - Expected to improve mechanical properties
  - Additional “smart” properties: electromagnetic field shielding, self-sensing capabilities, self control of cracks
  - Key aspects: proper dispersion and degree of interfacial interaction between the carbon nanofibers (CNFs) and the cement phases

Need for understanding the mechanisms of action of CNFs in cement pastes and the impact of their long-term use

Complex Interaction with the Environment



Weathering "forces" →

- Temperature (elevated, cyclic)
- Radiation (solar, nuclear, thermal)
- Freeze/thaw cycling
- Wetting/drying cycling
- Water (solid, liquid, vapor)
- Chloride attack (sea water, deicer salts)
- Acid attack (HCl, H_2SO_4, acetate,...)
- Sulfate attack (soil, sea water,...)
- Microbiological attack
- Air constituents (O_2, O_3, CO_2)
- Acidic air pollutants (NO_X, SO_X,...)

Internal chemical changes →

- Decalcification
- Slow hydrolytic decomposition of hydration products
- Desiccation / change in moisture
- Exchange reactions with cement paste
  - Formation of soluble/ insoluble Ca salts
  - Carbonation
  - Substitution reactions in CSH
- Reaction product accumulation, crystallization, and polymerization
- Alkali-silica reactions
- Activation / deactivation of fiber surface

Internal stresses →

Bulk cement paste

- Loss of alkalinity
- Increase in volume of crystallized phase
  - Increase in stresses
- Change in microstructure and morphology
- Shrinkage

Cement-fibers interface and interfacial zone

- Change in fiber surface properties
- Change in bond strength
- Change in local microstructure and morphology
- Local material loss
- Weakening of fiber

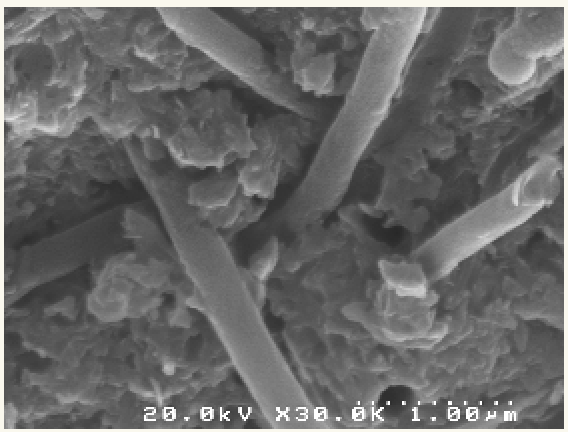
Material damage

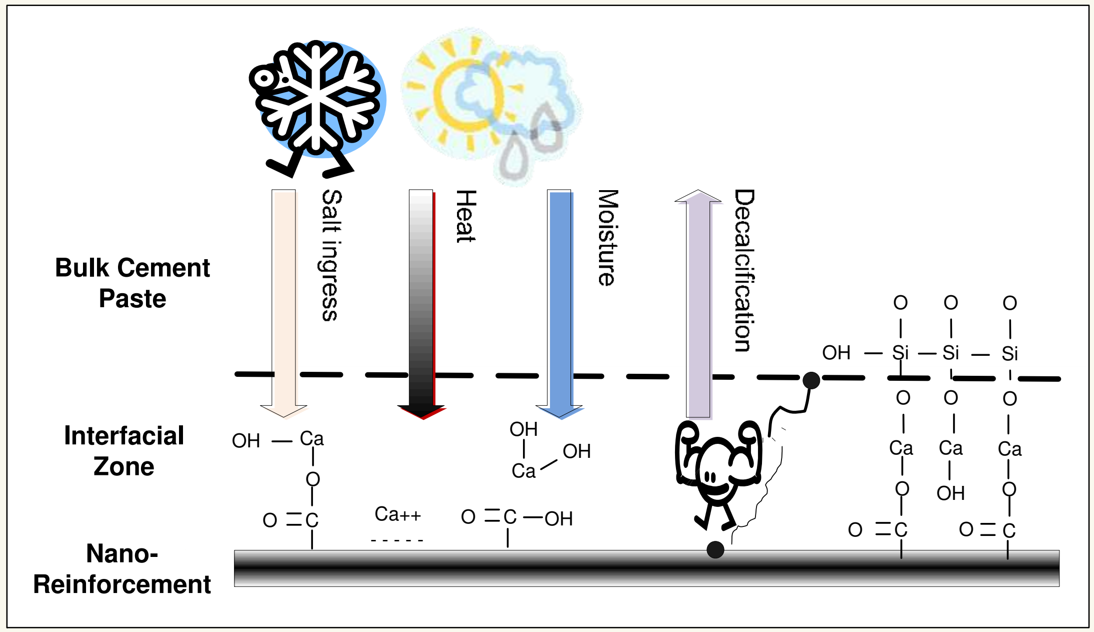
- Loss of compressive strength
- Loss of tensile strength
- Loss of mass
- Change in Young's modulus
- Change in fracture toughness
- Change in porosity
- Increase in permeability
- Deformation
  - Expansion
  - Cracking
  - Spalling
- Debonding
- Delamination

Increase in deterioration processes

Developed by F. Sanchez

Nano-Reinforcement/ Cement Interface





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Research Objectives

- Determine the effect of surface treatment and admixture addition on the incorporation of CNFs in cement composites
- Determine the effect of decalcification on the interface between CNFs and cement phases
- Investigate how microstructural and morphological alteration of the cement paste due to decalcification affects the role of the CNFs and in turn the macroscale properties of the material

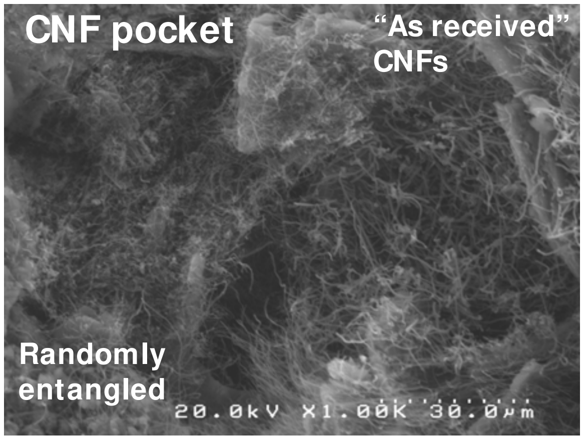
Materials

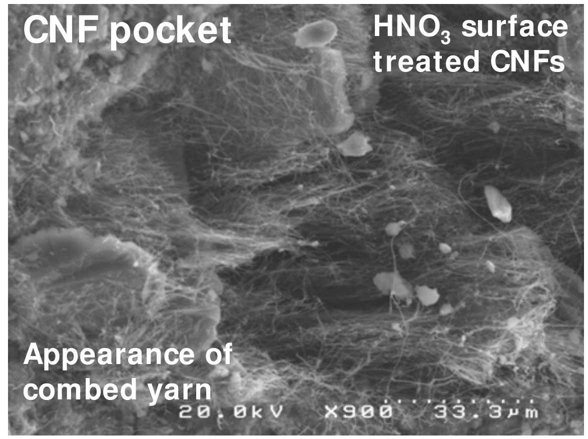
- Two types of cement pastes
  - Portland cement (PC)
  - Portland cement with 10 wt.% silica fume (SF)
- Carbon nanofiber (CNF) size
  - ~ 75-150 nm dia., 100-300 μm long
- Surface treatment: HNO_3
- Mix design
  - CNF loadings: 0 and 0.5 wt%
  - Water/cementitious material: 0.33
- Specimens
  - Cylinders – 2in dia. x 4in height
  - Curing – 28 days minimum, room temperature, 100% RH

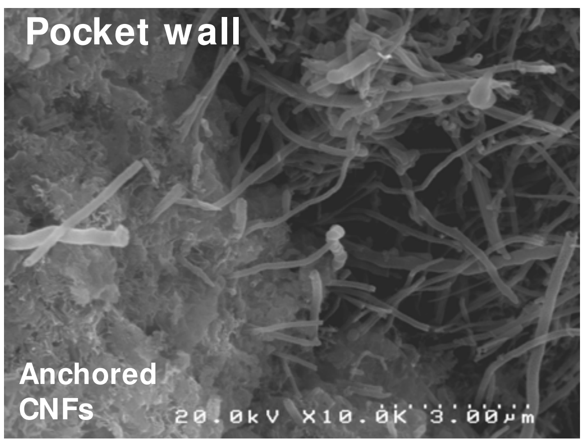
Microstructure Studies

CNF/ Portland Cement Composites

Int. J. Materials and Structural Integrity, In press



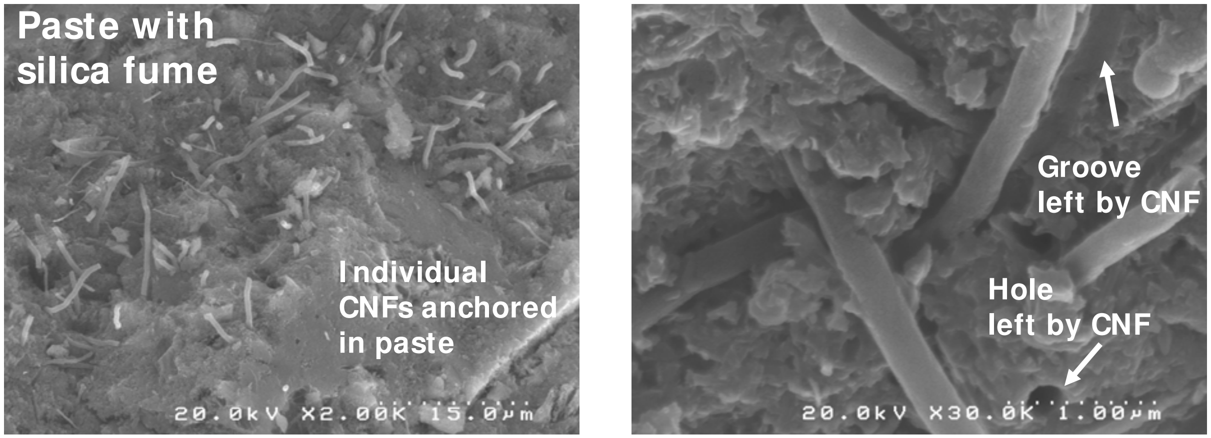




Entangled network of CNFs intermixed with hydration products

Microstructure Studies
CNF/ Cement Composites

Composites Science and Technology, 69 (2009) 1310–1318



- Individual CNFs well anchored inside of hydration products
- Silica fume facilitated CNF dispersion

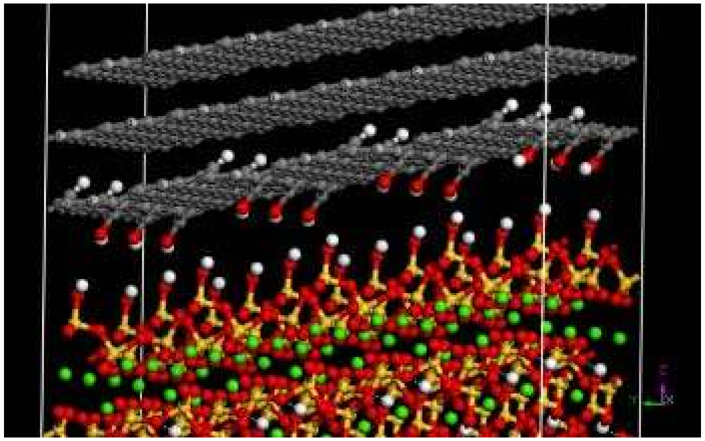
Microstructure Studies
CNF/ Portland Cement Composites

- CNFs found acting as bridges between hydrates
- Surface coating on CNFs

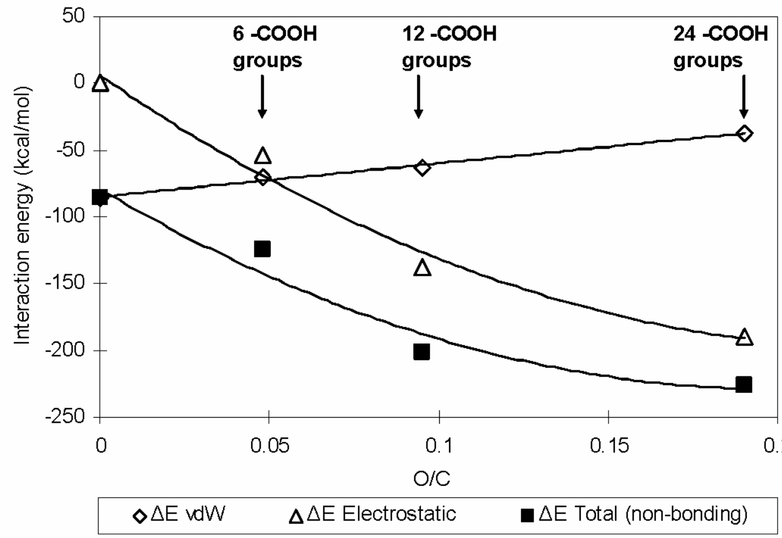
Interface Studies

Molecular Dynamics Modeling

J. of Colloid and Interface Science, 323 (2008) 349–358



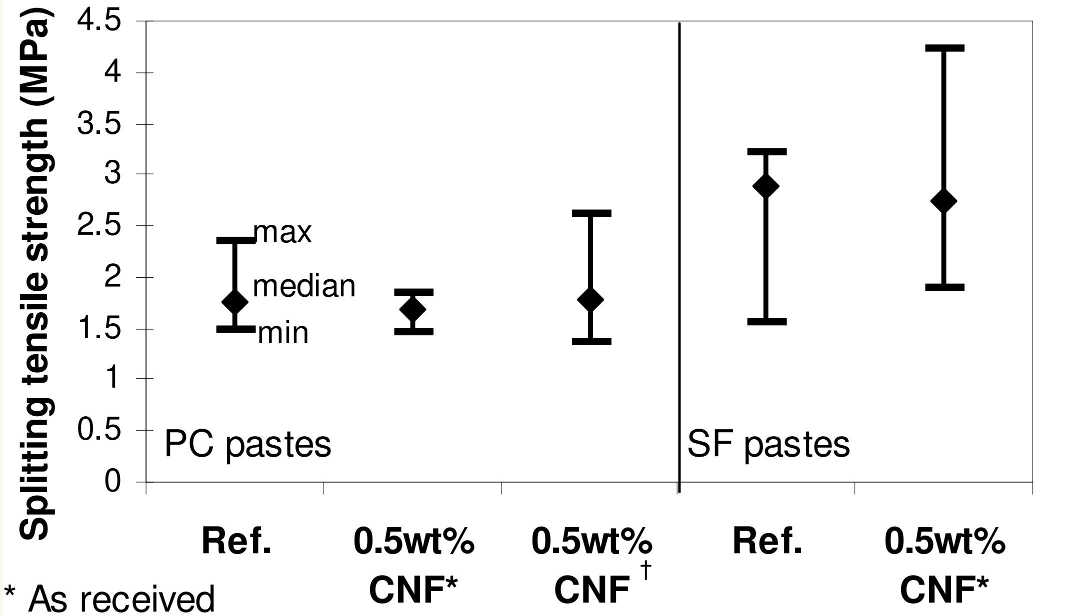
Polarity of functional group drives affinity to cement phases



- H-bond network developed across the interface, bridging the structures
- Optimal number of O-containing groups required for efficient graphitic structure/cement interaction

Macroscopic Property Studies

CNF/ Cement Composites



* As received

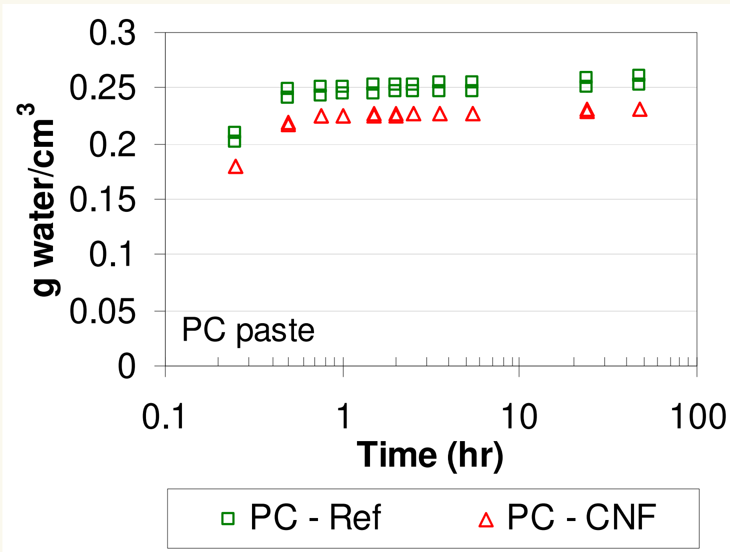
† Surface treated with nitric

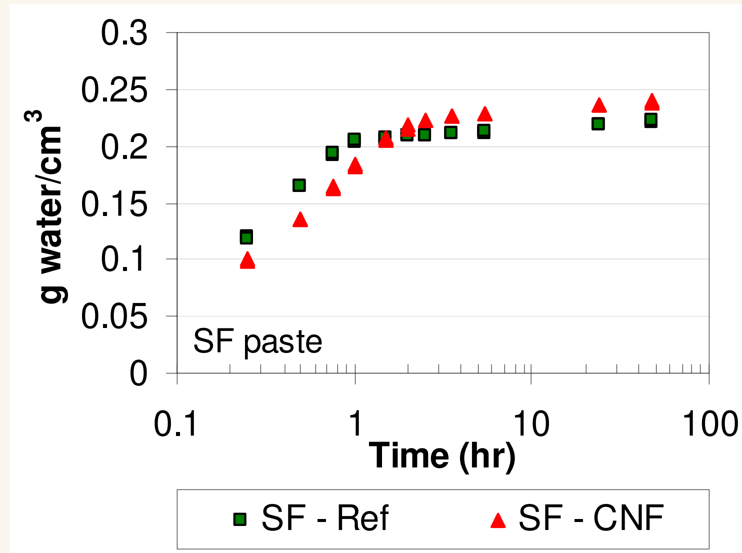
Post compression

Durability Studies

- Water absorption studies
- Decalcification studies
  - 7M NH_4NO_3 solution
  - Accelerates calcium leaching by formation of $Ca(NO_3)_2$
  - Liquid-to-Surface ratio = 5 mL/cm^2
  - Immersion: 7, 30 and 95 days - No renewal
- Material characterization
  - Mineralogical changes
    - Solid phase mineralogy and element mapping of leached cement pastes
  - Microstructural changes
  - Mechanical performance effect

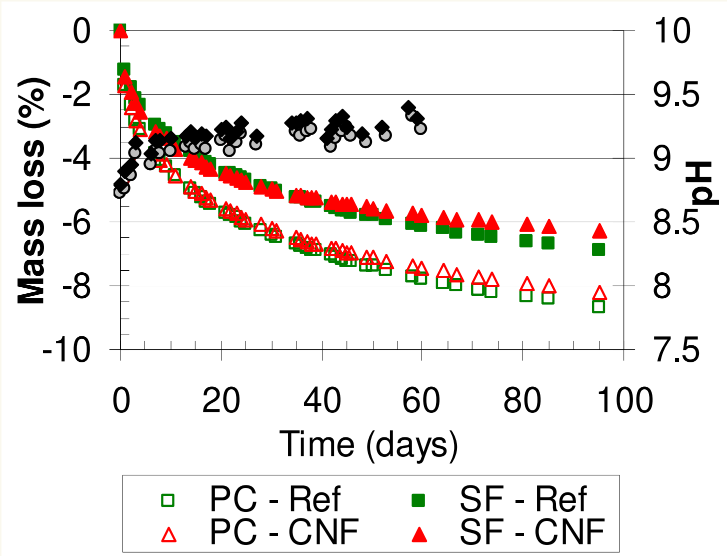
Water Absorption Capacity
CNF/ Cement Composites

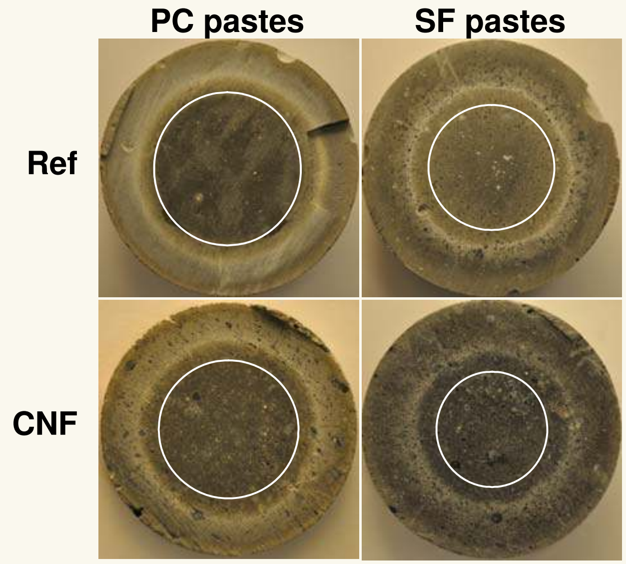




- PC paste – CNF pockets hydrophobic (Gore-Tex effect)
- SF paste – CNF pockets hydrophilic (C-S-H coating)

Mass Loss and Penetration Depth
CNF/ Cement Composites

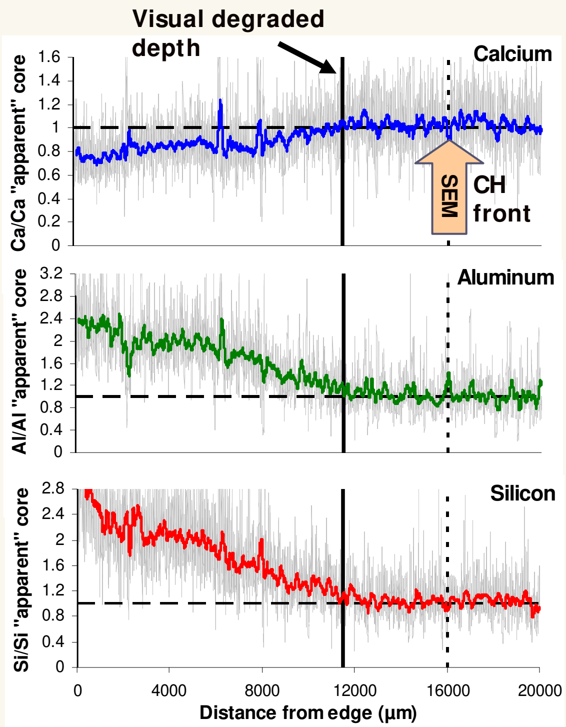


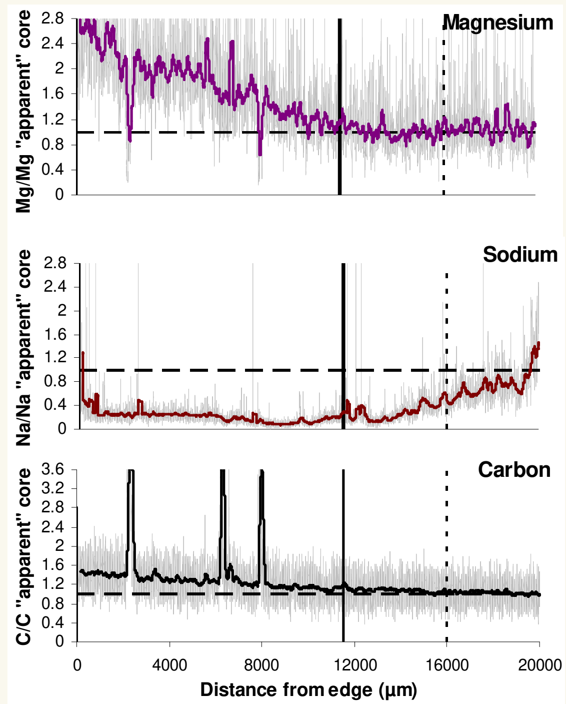


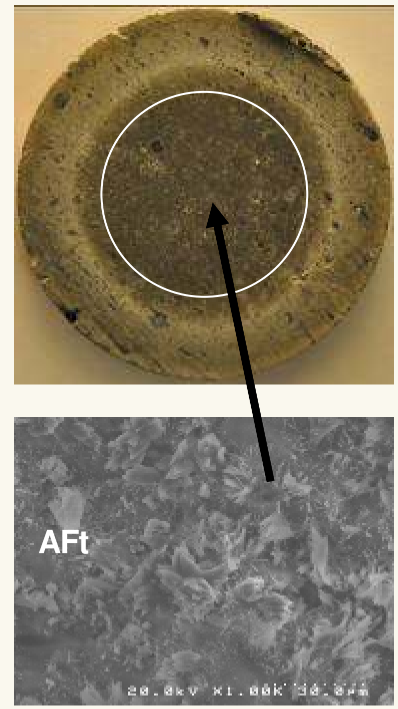
Exposure to NH_4NO_3 – 95 days

- Greater mass loss for PC pastes
- Greater visual degraded depth for SF pastes
- Greater visual degraded depth with CNFs
  - Influence of volume fraction of CNF pockets (~13% and 3%)

Element Mapping (LA-ICP-MS)
CNF/ Portland Cement Composite

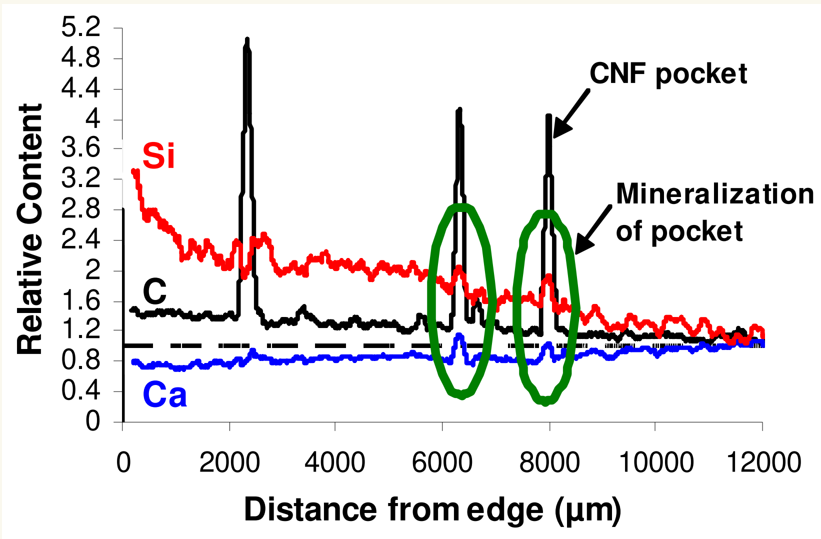


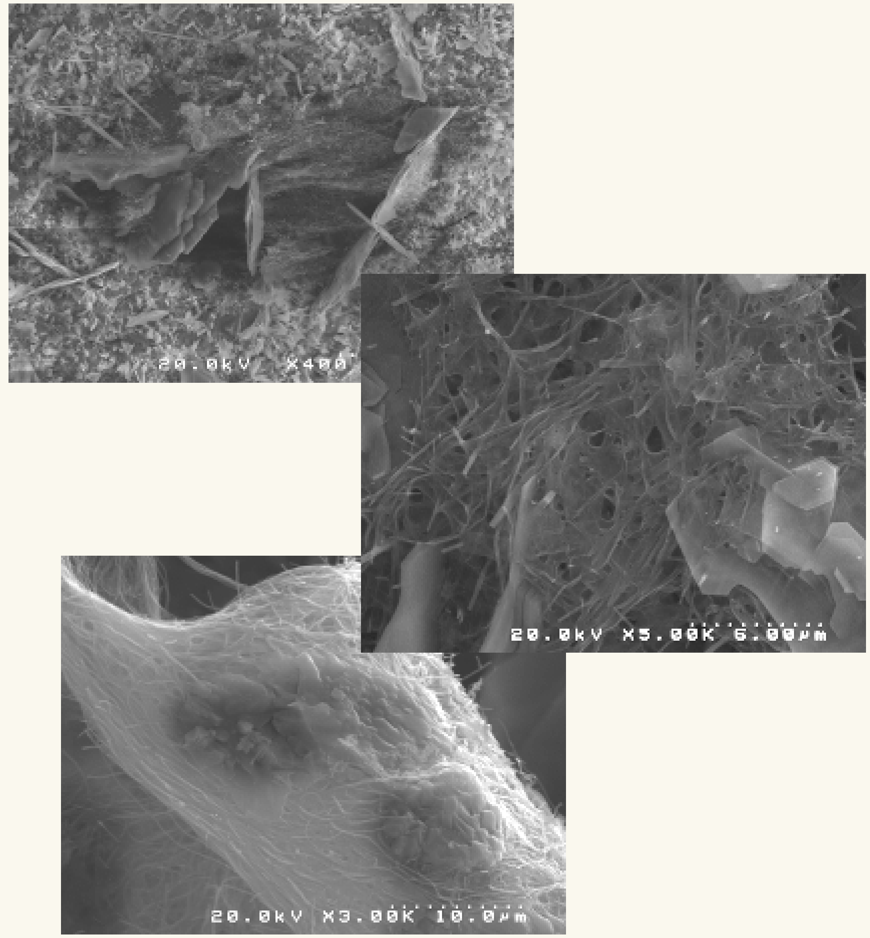




- Visual degraded depth did not provide complete delineation of degraded state of the paste
- "Sound zone" altered

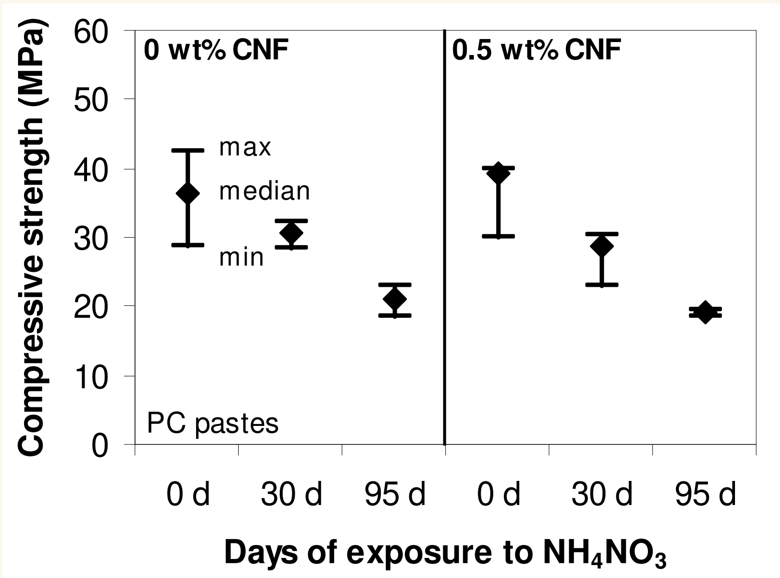
Mineralization of CNF Pockets
CNF/ Portland Cement Composite

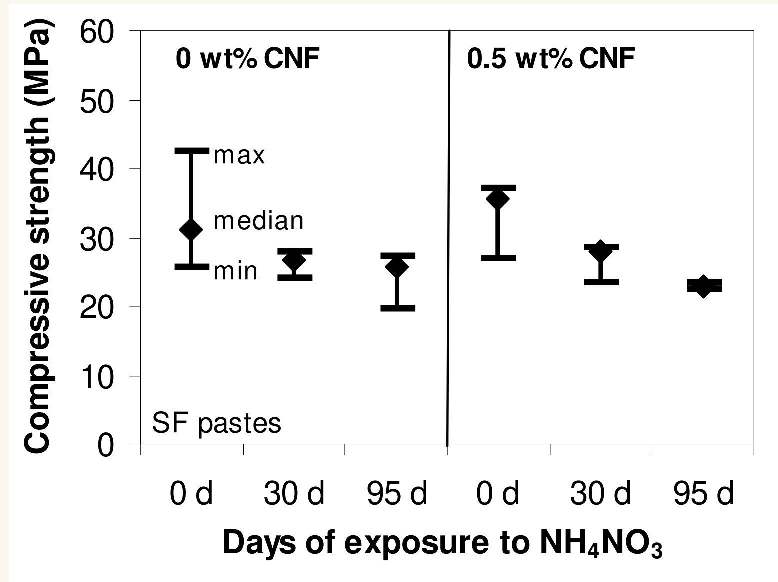




- CNF pockets acted as sink for Ca, Si, Al
- Impregnated CNF meshwork

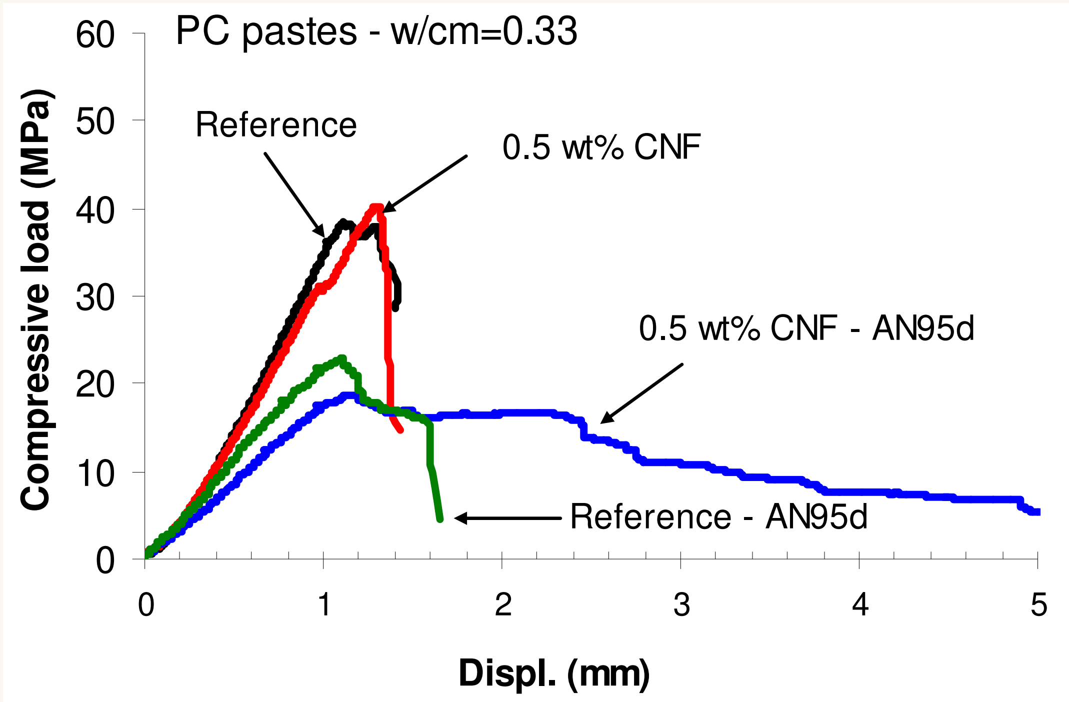
Mechanical Effect of Decalcification
CNF/ Cement Composites





- No residual effect of CNFs on ultimate compressive strength

Mechanical Effect of Decalcification
CNF/ Portland Cement Composites



- Decalcification resulted in a change in failure mode from brittle cracking to slow ductile load dissipation

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Conclusions

- SF and surface treatment with HNO_3 facilitated CNF dispersion and improved interfacial interaction
- Unchanged compression and tensile strengths with CNFs but residual load-bearing capacity post failure
- Hydrophobic/hydrophilic effect of CNF pockets
- Important role of CNF pockets in the decalcification process
  - Kinetics of degradation affected by volume fraction of CNF pockets
  - CNF pockets acted as sink for Ca, Si, Al
- Decalcification changed the failure mode from brittle cracking to slow ductile load dissipation, which was more pronounced for the PC paste with CNFs
- MD a useful technique for understanding interfacial interaction between cement phases and reinforcing structure

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