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Civil and Environmental Engineering



SCHOOL OF ENGINEERING





#### **Motivation**

- Increase interest in multi-functional, structural composites
  - Demand for smart structures with superior mechanical and functional properties
  - Importance of weight savings
- Nanofiber/cement composites
  - Expected to improve mechanical properties

Carbon nanofibers

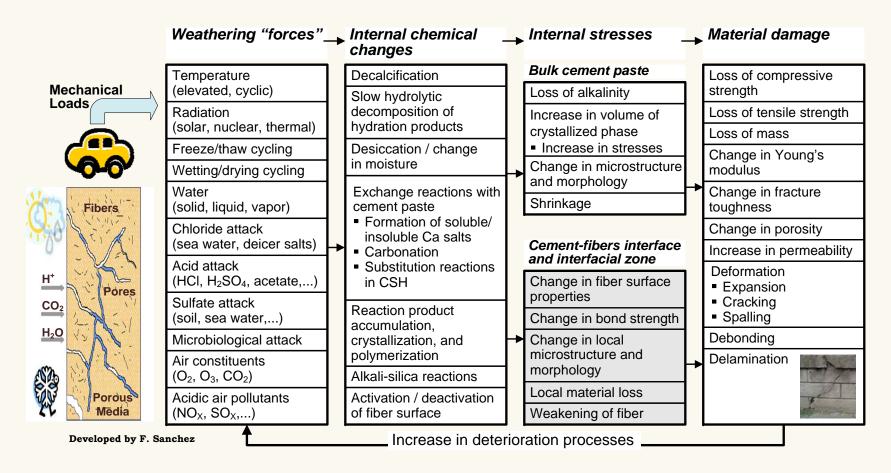
- Additional "smart" properties: electromagnetic field shielding, self-sensing capabilities, self control of cracks
- Key aspects: proper dispersion and degree of interfacial interaction between the carbon nanofibers (CNFs) and the cement phases

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

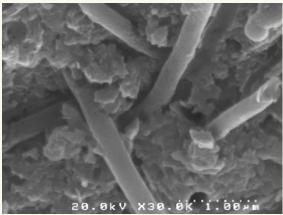


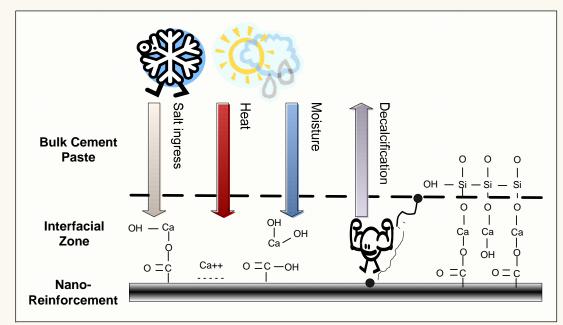




#### Nano-Reinforcement/Cement Interface











#### **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
  - $\sim 75-150$  nm dia., 100-300  $\mu$ m long
- Surface treatment: HNO<sub>3</sub>
- 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



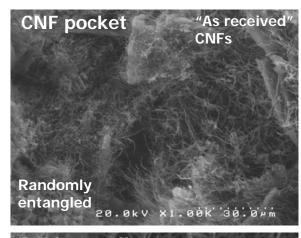


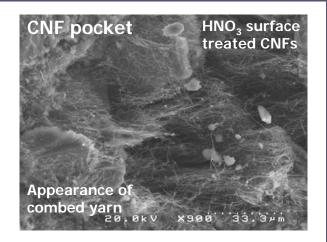


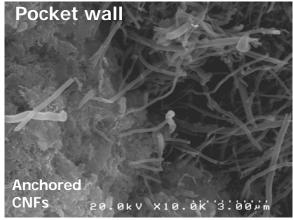


## Microstructure Studies CNF/Portland Cement Composites

Int. J. Materials and Structural Integrity, In press







Entangled network of CNFs intermixed with hydration products

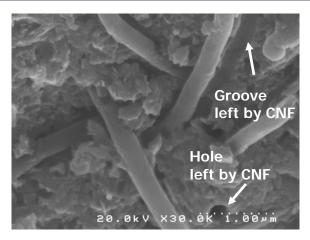




### Microstructure Studies CNF/Cement Composites

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



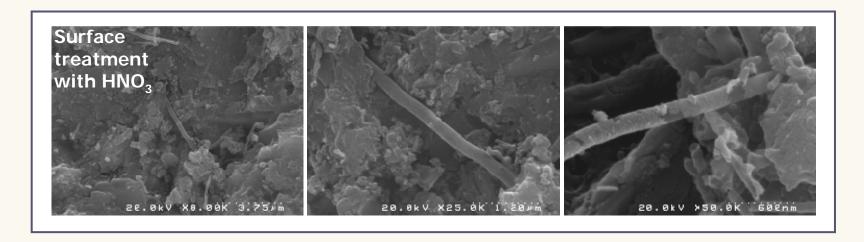


- Individual CNFs well anchored inside of hydration products
- Silica fume facilitated CNF dispersion





## Microstructure Studies CNF/Portland Cement Composites



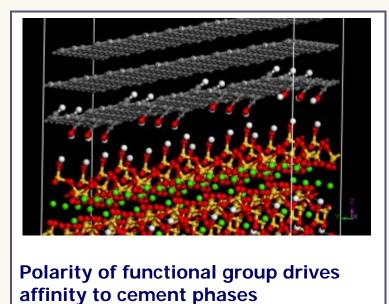
- CNFs found acting as bridges between hydrates
- Surface coating on CNFs

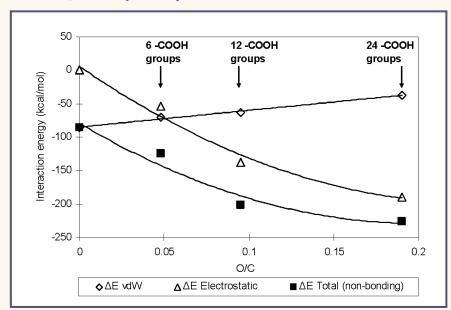




## Interface Studies Molecular Dynamics Modeling

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



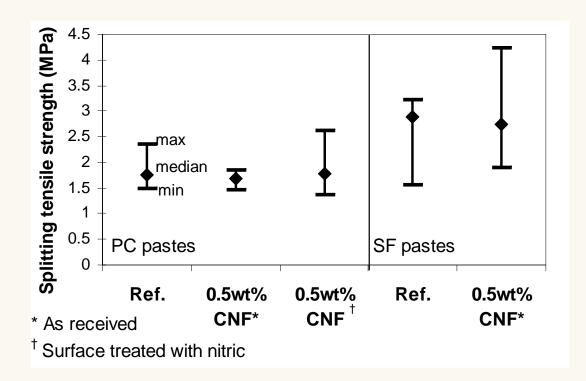


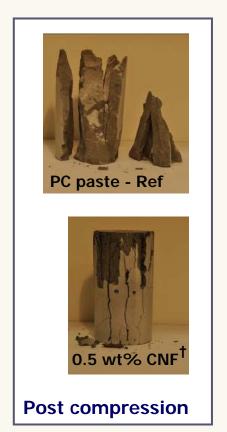
- H-bond network developed across the interface, bridging the structures
- Optimal number of O-containing groups required for efficient graphitic structure/cement interaction





## Macroscopic Property Studies CNF/Cement Composites









### **Durability Studies**

- Water absorption studies
- Decalcification studies
  - 7M NH<sub>4</sub>NO<sub>3</sub> solution
  - Accelerates calcium leaching by formation of Ca(NO<sub>3</sub>)<sub>2</sub>
  - Liquid-to-Surface ratio = 5 mL/cm<sup>2</sup>
  - 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

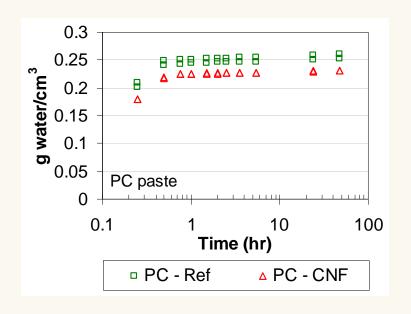


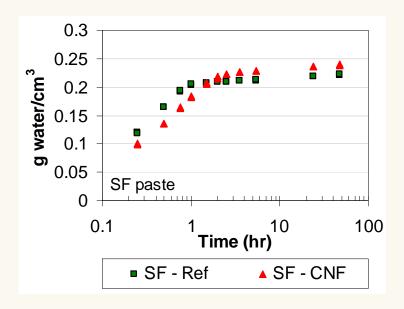






### Water Absorption Capacity CNF/Cement Composites



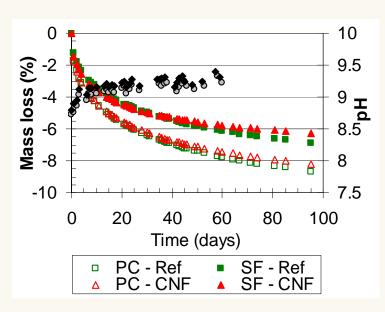


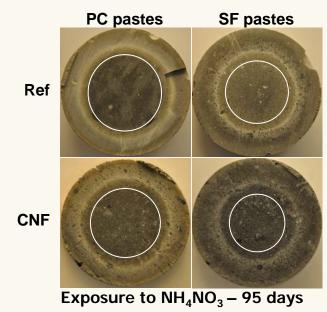
- PC paste CNF pockets hydrophobic (Gore-Tex effect)
- SF paste CNF pockets hydrophilic (C-S-H coating)





## Mass Loss and Penetration Depth CNF/Cement Composites



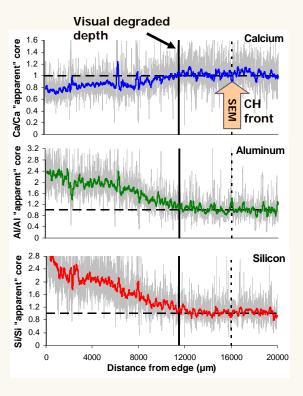


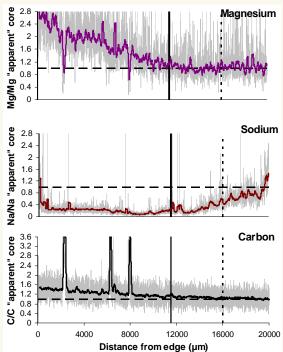
- Greater mass loss for PC pastes
- Greater visual degraded depth for SF pastes
- Greater visual degraded depth with CNFs
  - Influence of volume fraction of CNF pockets (~13% and 3%)

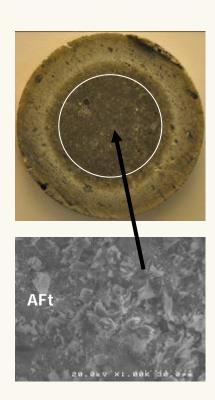




## **Element Mapping (LA-ICP-MS) CNF/Portland Cement Composite**





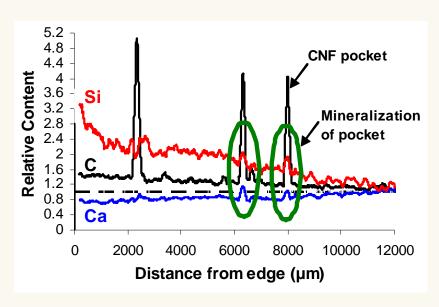


- Visual degraded depth did not provide complete delineation of degraded state of the paste
- "Sound zone" altered

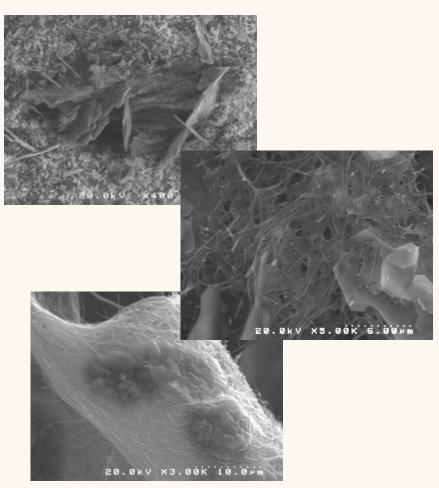




# Mineralization of CNF Pockets CNF/Portland Cement Composite



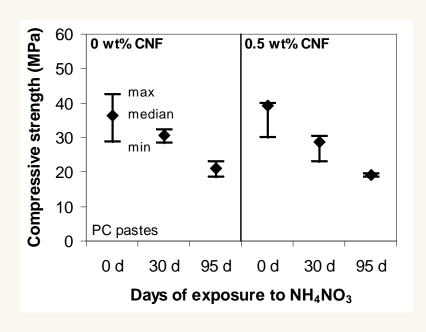
- CNF pockets acted as sink for Ca, Si, Al
- Impregnated CNF meshwork

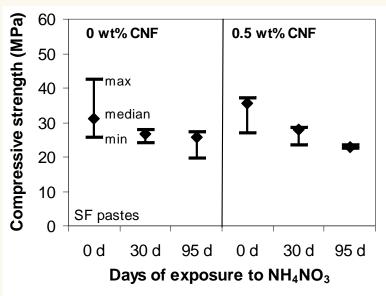






#### Mechanical Effect of Decalcification CNF/Cement Composites



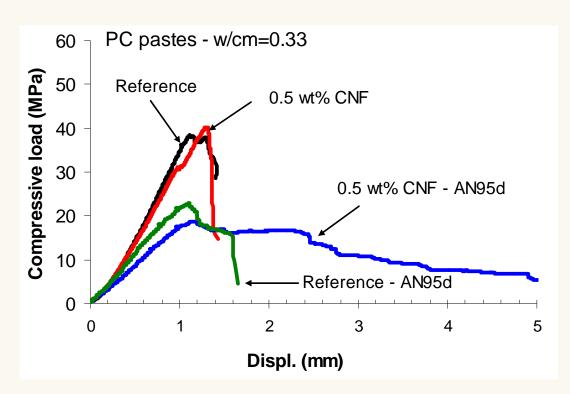


 No residual effect of CNFs on ultimate compressive strength





### Mechanical Effect of Decalcification CNF/Portland Cement Composites



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





#### Conclusions

- SF and surface treatment with HNO<sub>3</sub> 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





### **Acknowledgements**

- National Science Foundation (CMMI-0510534)
- Rossane Delapp, Senior Research Scientist
- David Delapp, Ph.D., Senior Research Engineer