Effect of Decalcification on the Performance of Carbon Microfiber Reinforced Cement-Based Materials

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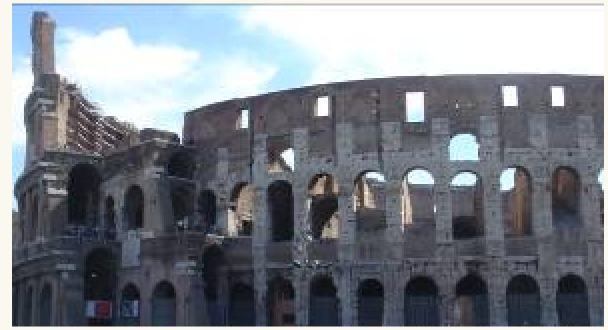
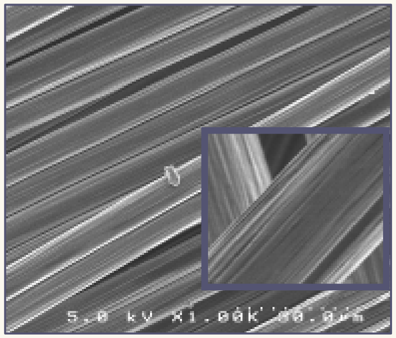
Motivation

- World most ubiquitous material
  - Invented more than 2,000 years ago
  - Billions of tons of concrete used each year
    - Buildings, highways, bridges, dams, sidewalks, artwork, waste containment systems
- Concrete infrastructure degradation
  - Common types of deterioration: loss of strength, cracking, expansion, spalling
  - Repeated fatigue loads, freezing/thawing, attack by a variety of natural and industrial chemicals



Motivation

- Microfiber reinforced cement-based materials
  - Expected to improve mechanical properties
  - Additional “smart” properties: electromagnetic field shielding, self-sensing capabilities, self control of cracks
  - Open the door for new applications, including nuclear waste containment
  - Most research on direct structural, mechanical, and electrical properties – Relates primarily to short term behavior

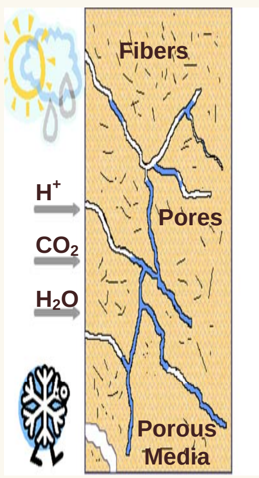


Carbon microfibers

Need for understanding the impact of their long-term use and the modes by which they progress toward failure

Complex Interaction with the Environment

Mechanical Loads



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

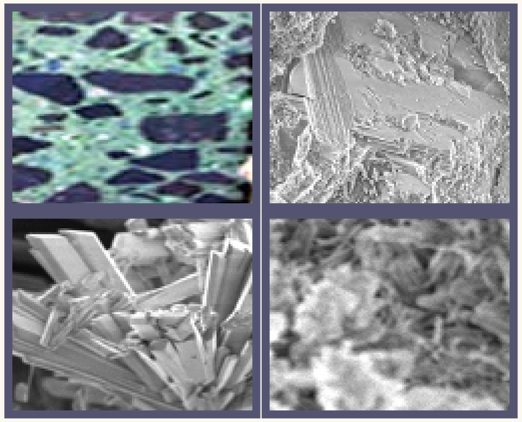
- Loss of compressive strength
- Loss of tensile strength
- Loss of mass
- Change in Young's modulus
- Change in fracture toughness
- Change in porosity
- Increase in permeability
- Deformation
  - Expansion
  - Cracking
  - Spalling
- Debonding
- Delamination

Increase in deterioration processes

Developed by F. Sanchez

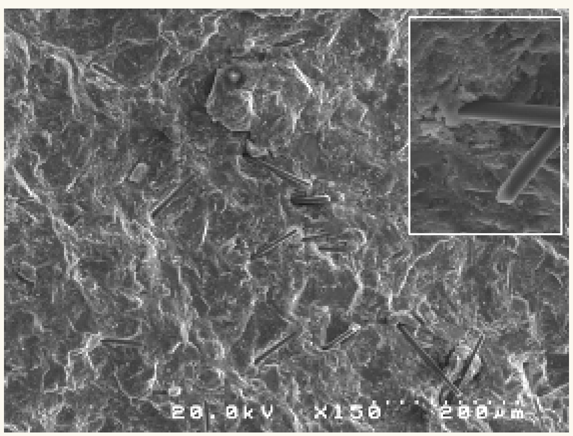
Concrete: A Nano-Structure Material

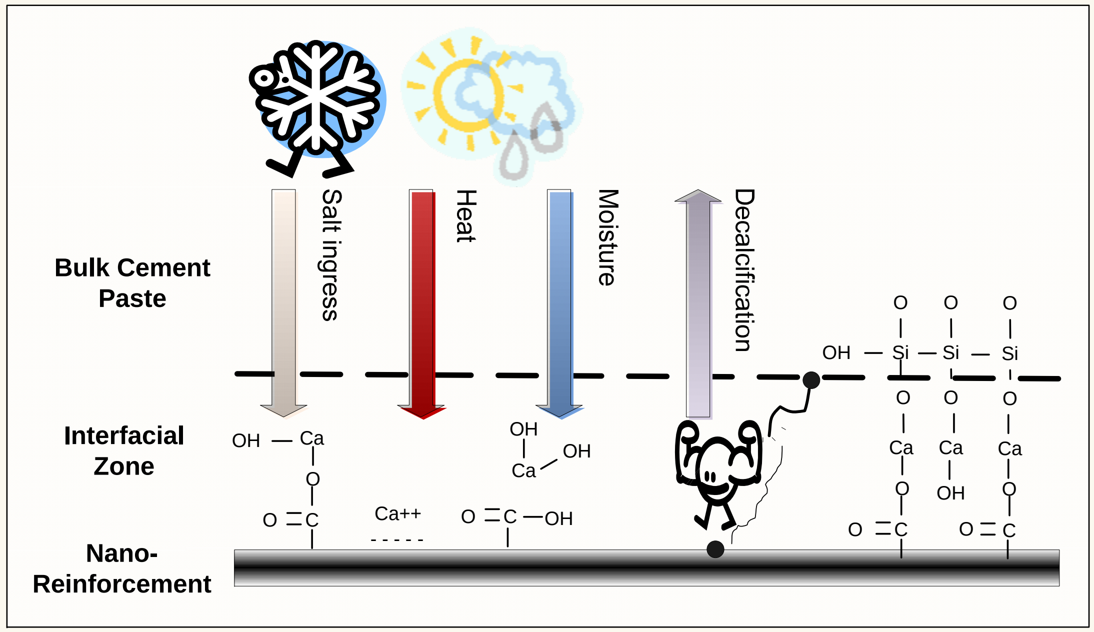
- Complex nanoscale structure
  - $Ca(OH)_2$, Calcium-Silicate-Hydrate, ettringite
  - Multi-size (nano to few millimeters)
  - Multi-phase (gels, crystals, water, air)
  - Ages over time due to reaction kinetics and environmental weathering events



- Engineering properties of the material depend on processes occurring at the nano-scale
  - Nano – molecular assemblages, fiber surfaces, and chemical bonds
  - Micro – fibers, hydration products, and capillary porosity
  - Macro – cement paste, aggregates, and voids

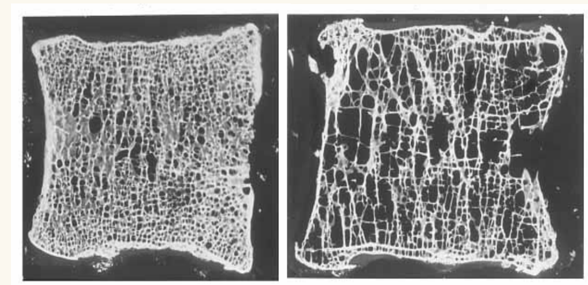
Micro-Reinforcement/Cement Interface

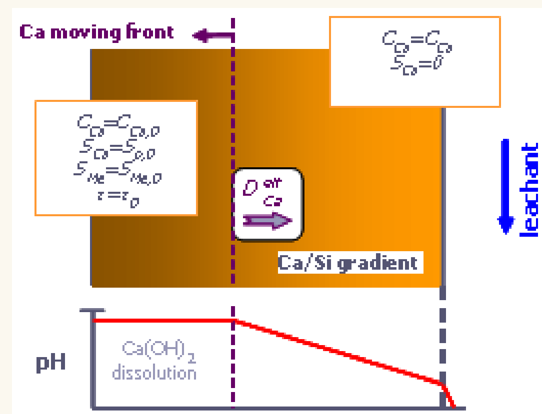




Decalcification or Loss of Calcium

- Closely associated with various types of cementitious material deterioration
  - Leaching by exposure to water or weak acids
  - Chemical attack such as sulfate or chloride attack
- Multiple overlapping processes
  - Dissolution-diffusion with sharp dissolution fronts
  - Dissolution of $Ca(OH)_2$
  - Removal of calcium from the C-S-H leading to a Ca/Si ratio gradient
- Leads to degradation of mechanical and physical properties
  - Increase in porosity
  - Loss of strength





Integrated Framework

Exchange with surrounding environment

Weathering

Mass Transfer

Diffusivity Porosity Cracks	*Multi-component diffusive transport models*

Material Chemistry

Equilibrium thermodynamics, Kinetics, Reaction energies, Chemical speciation	*Geochemical speciation models*
Multiphase interactions **Nano-reinforcement/cement interactions**	*Molecular dynamics models*

Internal chemical changes

Macroscale Properties

Compressive strength Tensile strength Young's modulus Tortuosity	*Macro-mechanical/ structural models*

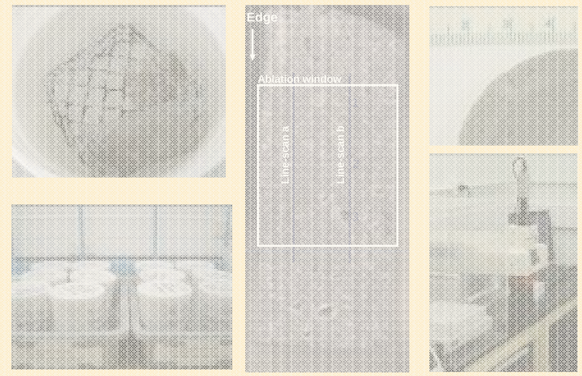
Micromechanical Stresses

Microstructure	*Micro-mechanical/structural models*
Interfacial shear stress Local Young's moduli	*Constitutive relationships* *Chemical-mechanical properties*

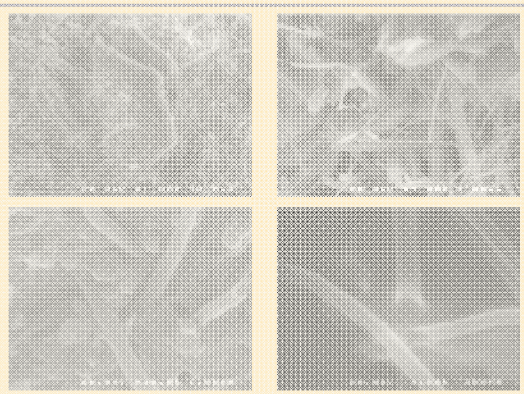
A Multi-Scale Experimental and Computational Characterization Program

Macroscopic Properties Studies

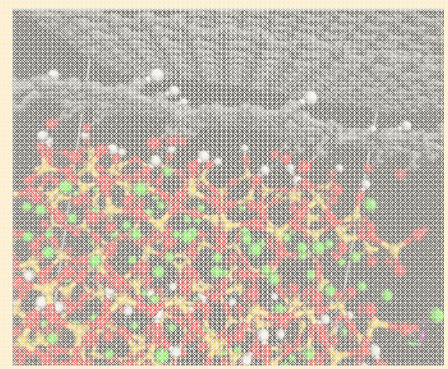
Durability Studies



Microstructure Studies



Interface Studies



Research Objectives

- Determine the effect of decalcification on the interface between carbon fibers and cementitious materials
- Investigate how microstructural and morphological alteration of the cement paste due to decalcification affects the role of the fibers 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 microfiber (CF) size
  - ~7 μm dia., 3-6 mm long
- Mix design
  - CF 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% relative humidity

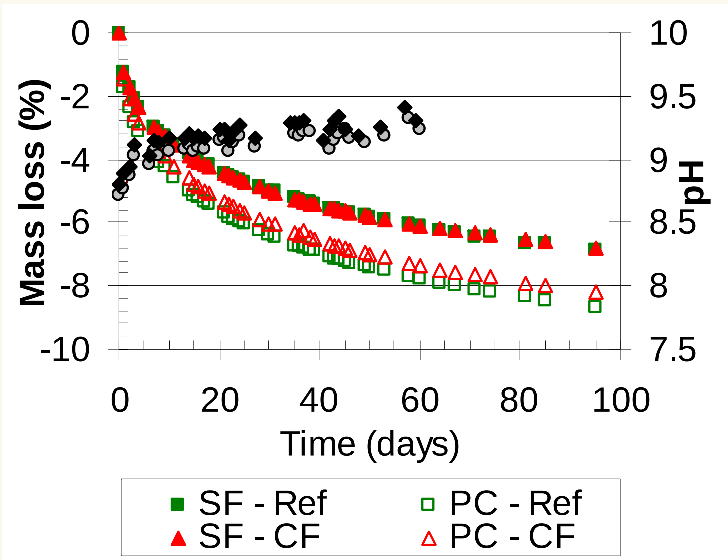
Decalcification

- Tank leaching in NH_4NO_3 solution
  - Accelerates calcium leaching by formation of $Ca(NO_3)_2$
  - 7M NH_4NO_3 solution
  - 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

Mass Loss and Penetration Depth

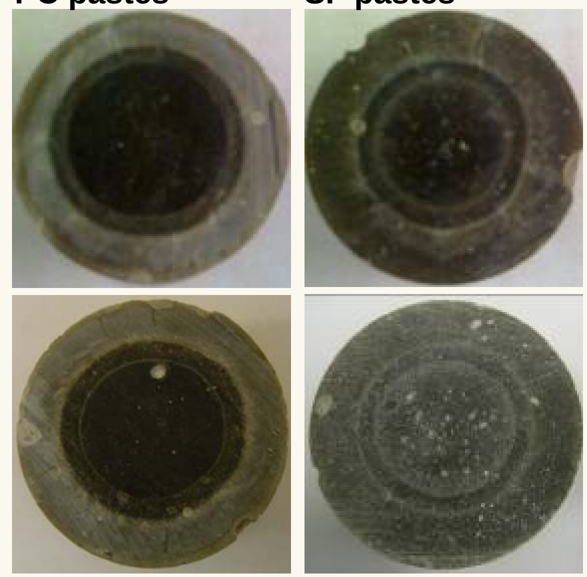
CF/Cement Composites



PC pastes SF pastes

Ref

CF



Exposure to NH_4NO_3 – 95 days

- Greater mass loss for PC pastes
- Greater “apparent” degraded thickness for the SF pastes
- “Apparent” degraded thickness in contrast with mass loss

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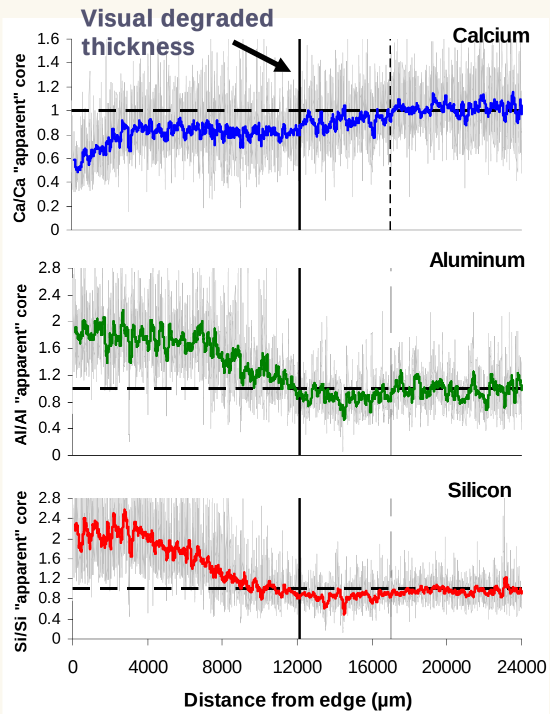
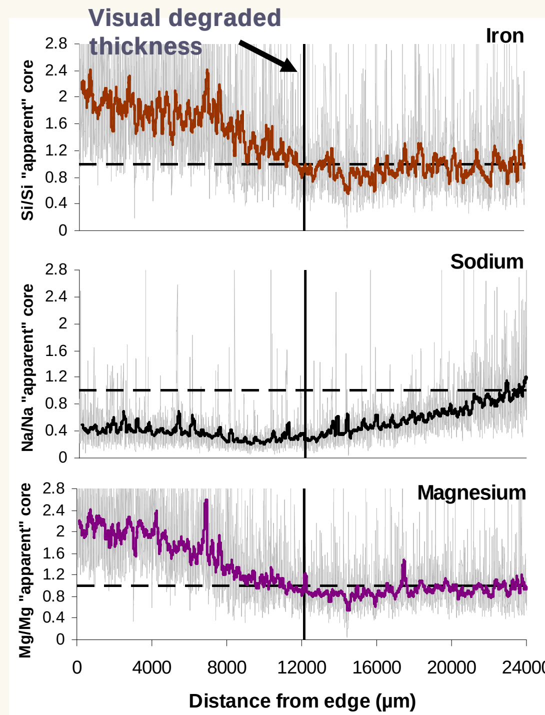
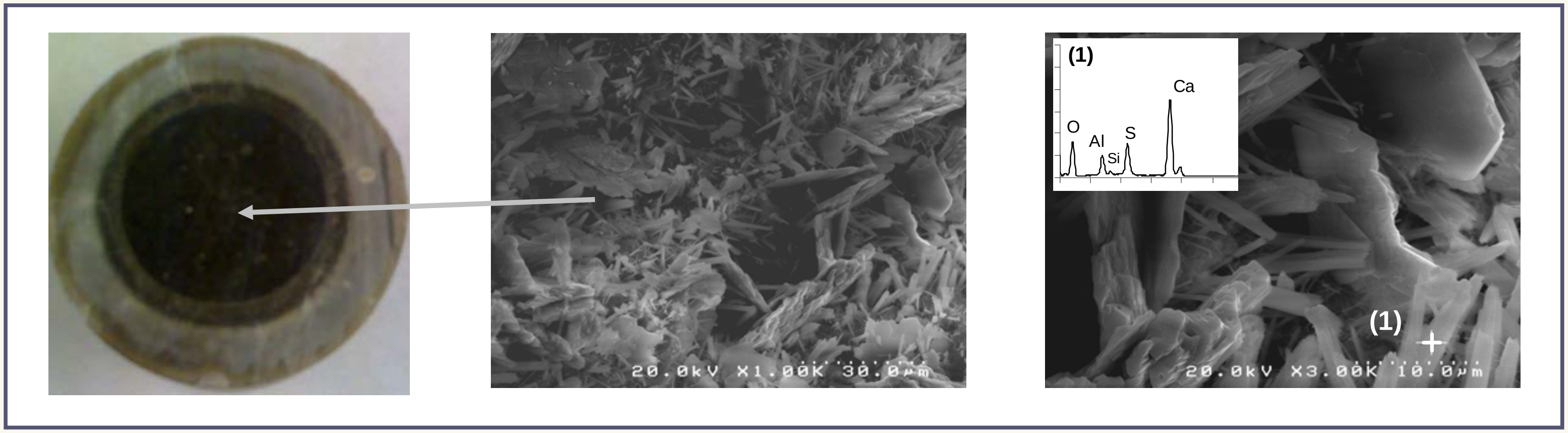
Element Mapping (LA-ICP-MS)
CF/PC Composites





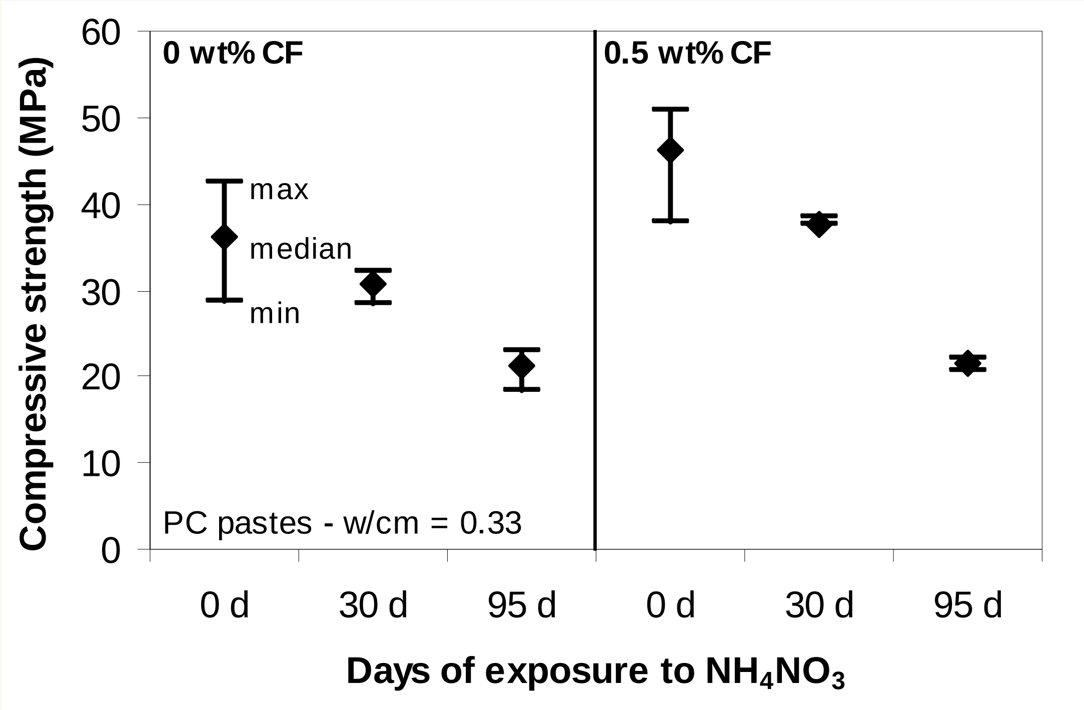
- Visual degraded thickness did not provide correct delineation of degraded state of the paste
- "Sound zone" most likely altered

Microstructure
CF/PC Composites



- Significant presence of needle-like ettringite seen in the "sound-zone"

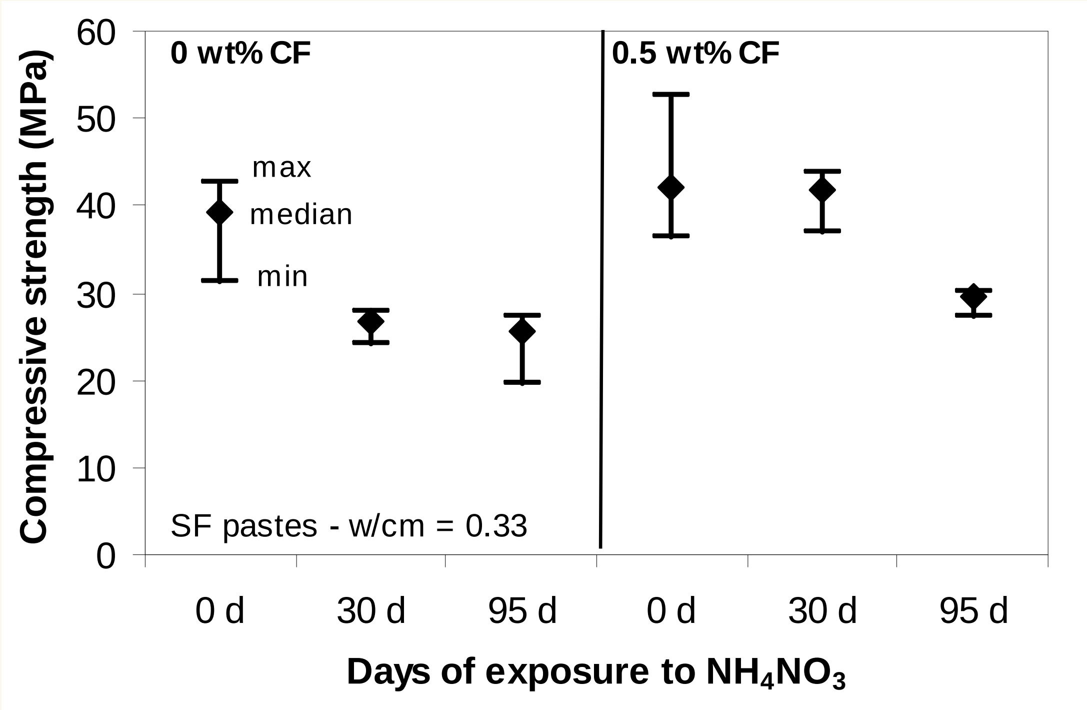
Mechanical Properties
CF/PC Composites



- Greater loss in strength for paste reinforced with 0.5 wt% CFs
- Fiber debonding and loss of cohesion at the interface

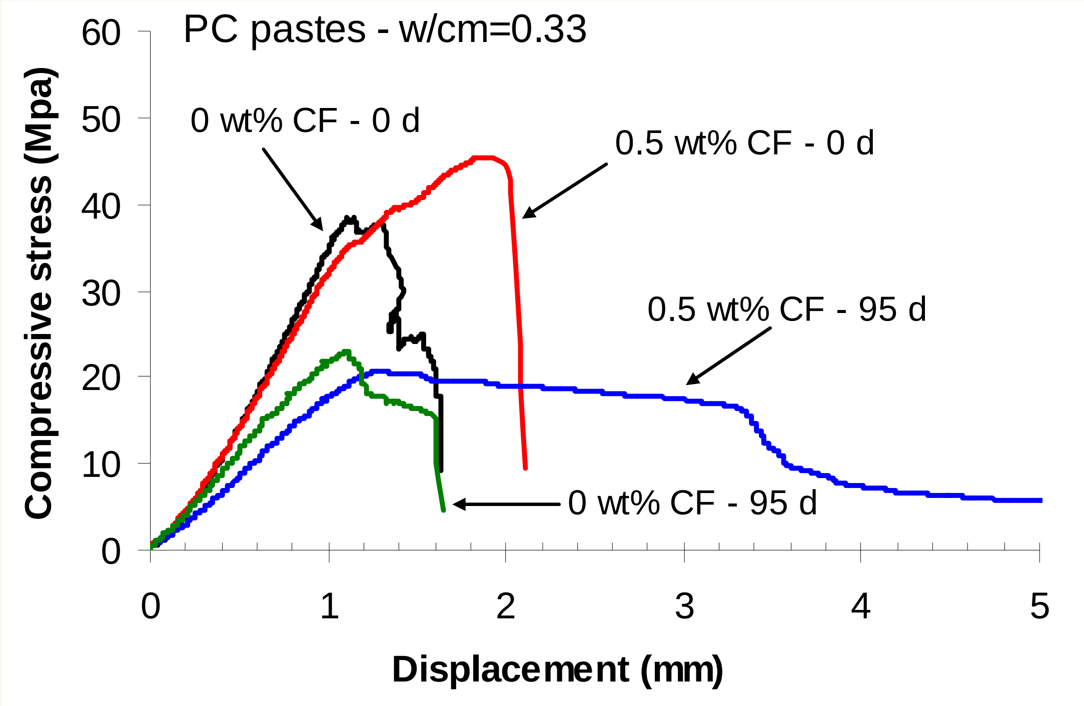
Mechanical Properties

CF/SF Composites



- Decalcification had a lesser effect on the compressive strength than for the PC paste

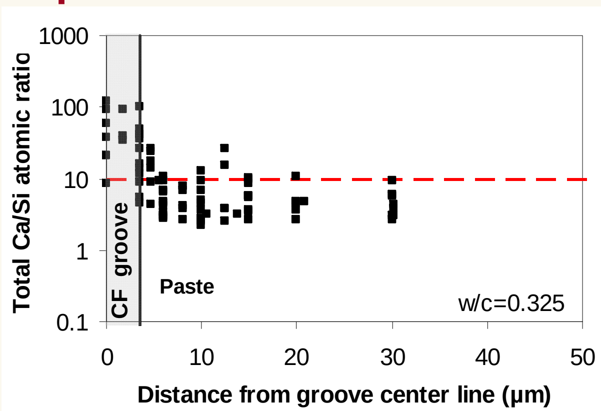
Mechanical Properties
CF/PC Composites

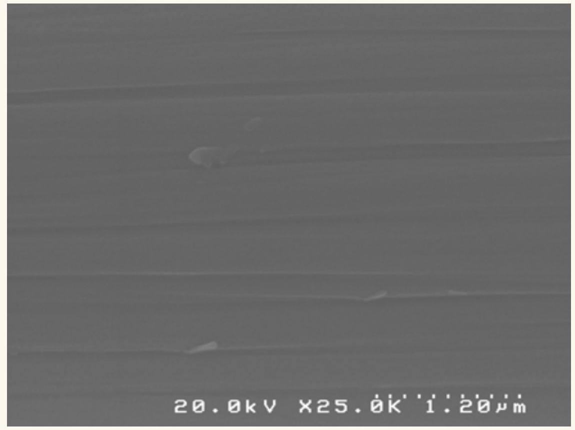


- Decalcification resulted in a change in failure mode from brittle cracking to slow ductile load dissipation

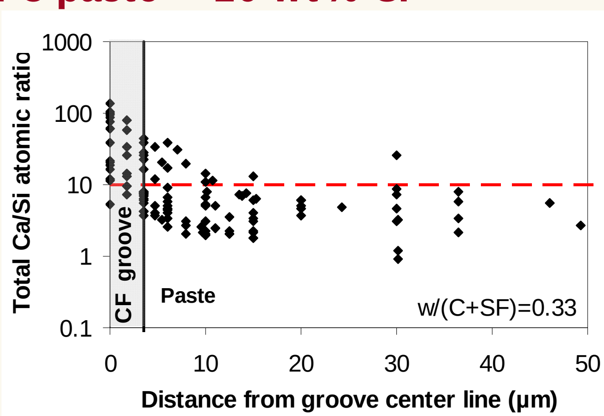
Interface Studies
CF/PC Composites

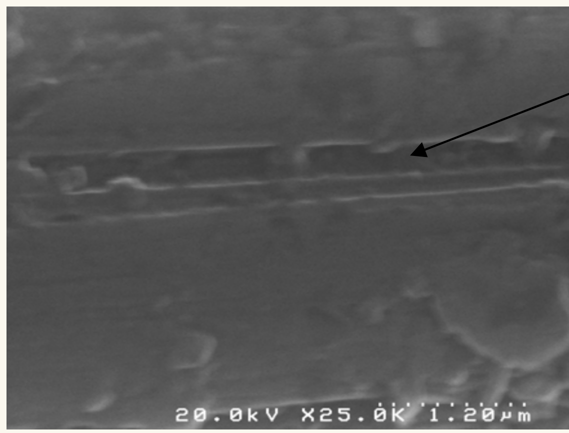
PC paste

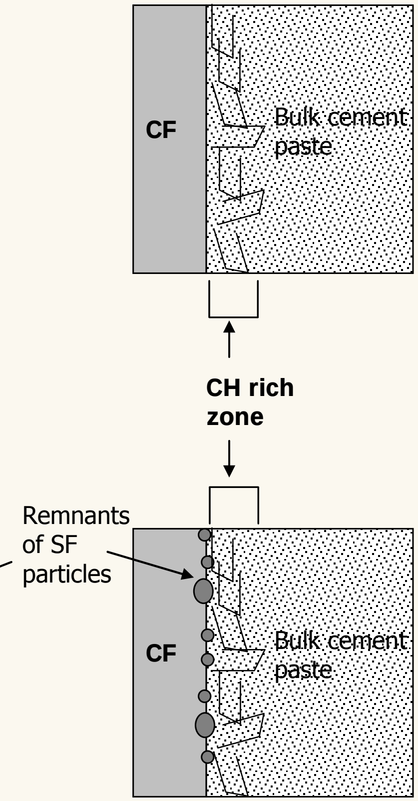




PC paste + 10 wt% SF



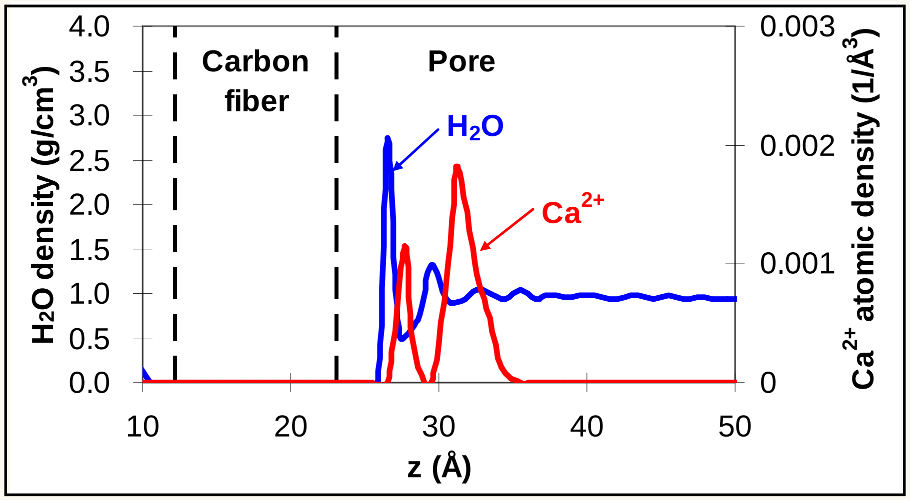


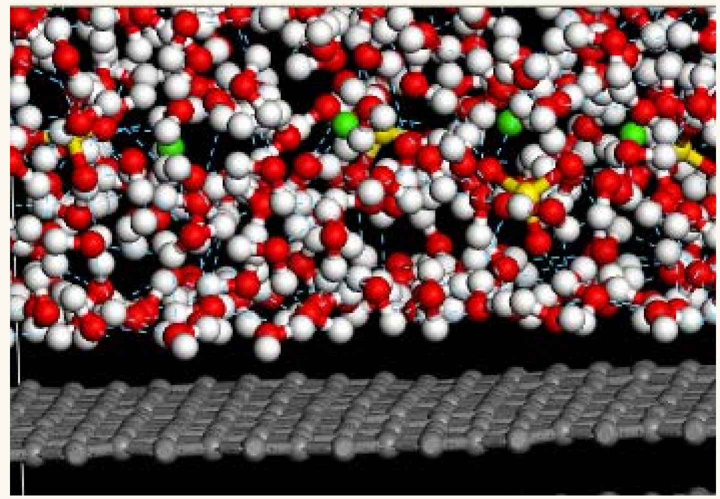


Schematic representation of the fiber-cement interface

Interface Studies
MD modeling

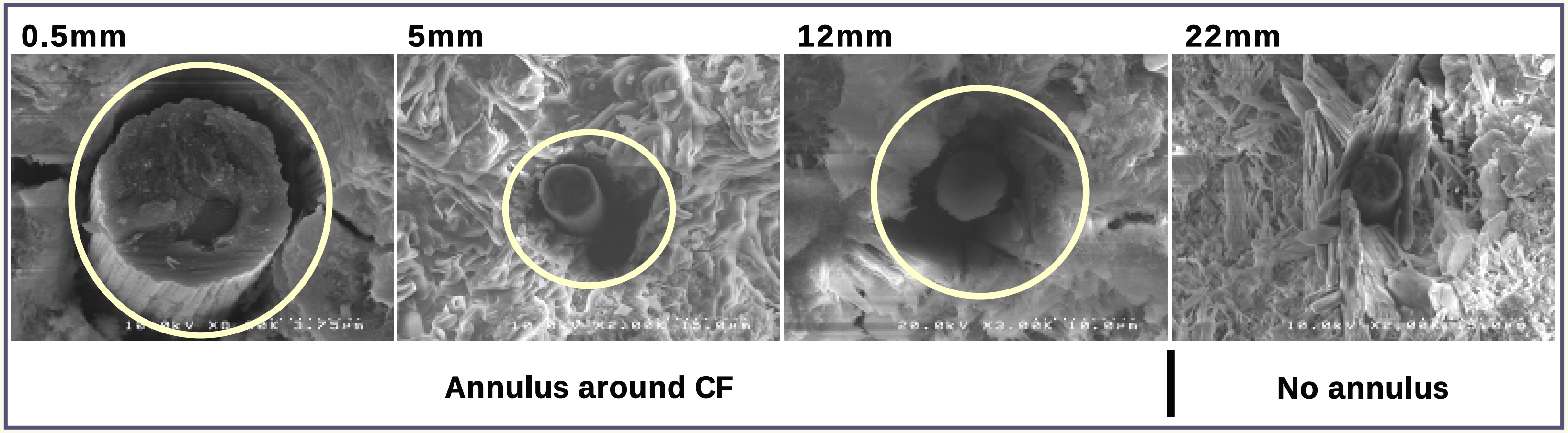
Submitted for publication to Carbon, March 2009





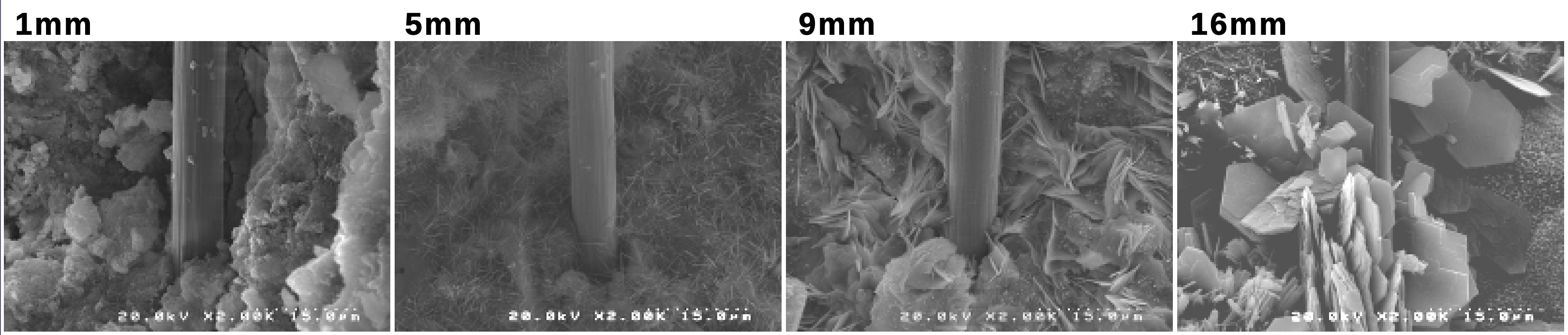
- Ordering of H_2O molecules near graphite surfaces
- Ca^{2+} ions intercalated between the layers of H_2O or outside the second H_2O layer

Interface Studies
CF/PC Composites



- Preferential leaching at the fiber-cement interface for the PC paste

Interface Studies
CF/SF Composites

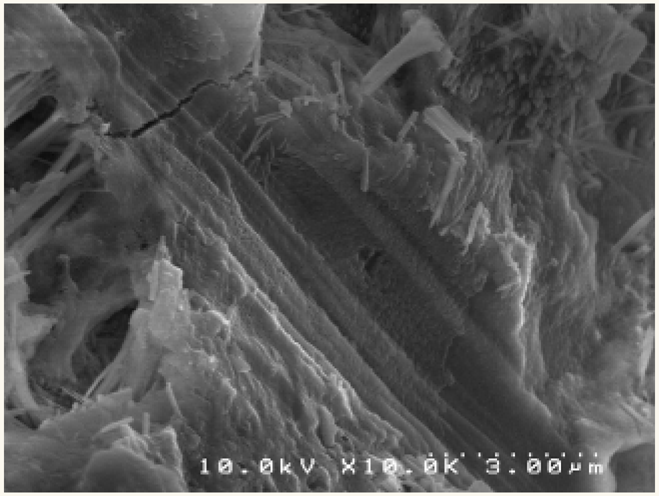


No annulus

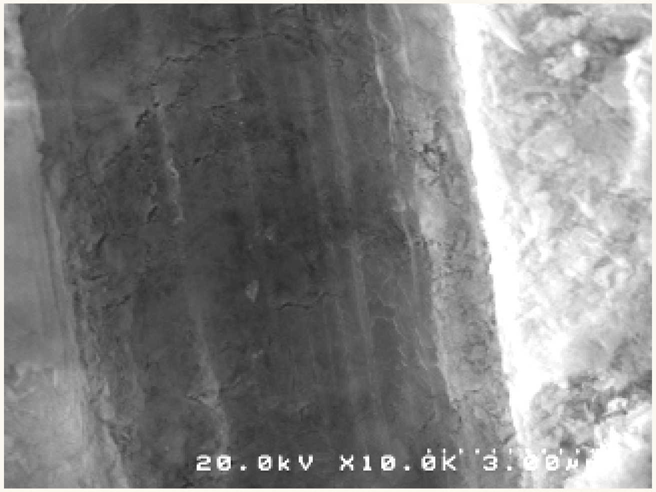
- Evolution of the interface in the SF paste was different from the PC paste
- No annulus at the fiber-cement interface found

Interface Studies
CF/Cement Composites

PC paste



SF paste



- Different groove weathering between the PC and SF pastes

Conclusions

- The visual degraded thickness did not correspond to the actual degradation depth of the pastes
- The interface morphology between the fiber and the cement paste was a function of degradation depth
- The morphology and evolution of the interface was different for the PC and SF pastes
- Preferential leaching can occur around the fibers, resulting in debonding and greater loss of strength for the PC paste
- Decalcification changed the failure mode from brittle cracking to slow ductile load dissipation, which was more pronounced for the PC paste with fibers

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