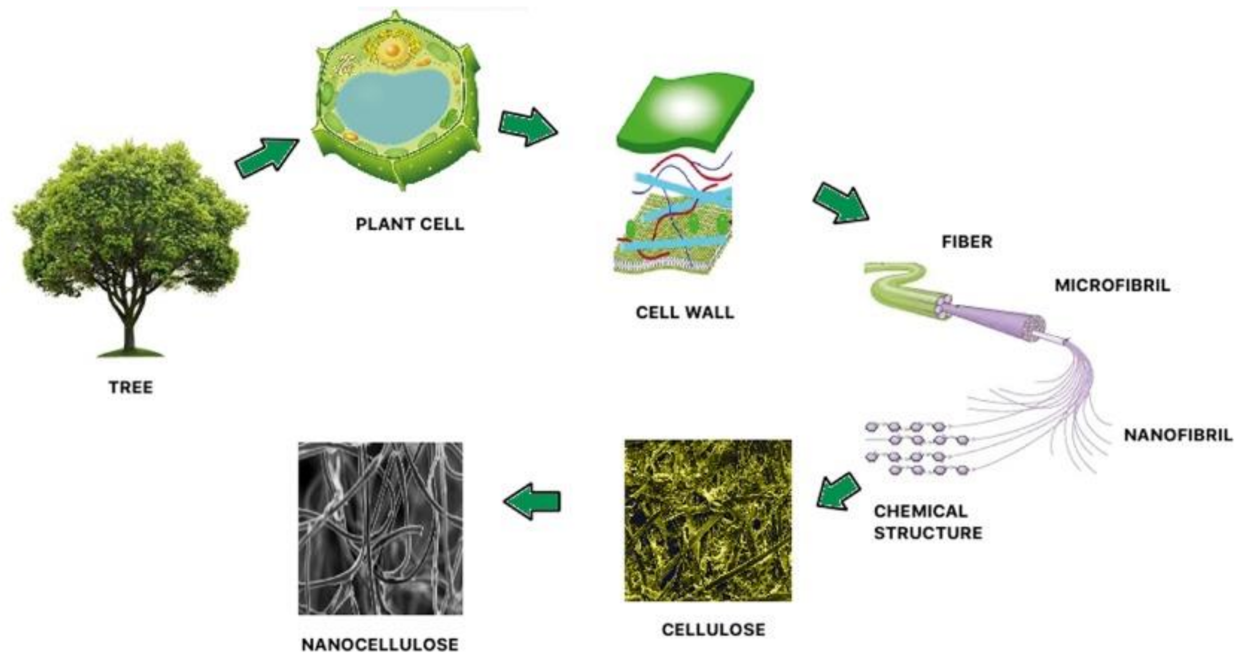
# Application of Bio Based Nano Fibers as Mechanical and Durability Performance Enhancements for Cement Based Composites

***Nithya Nair, Warda Ashraf , Surendra Shah***
Department of Civil Engineering, University of Texas at Arlington

# Background: Cellulose Nanofibers

❖ Cellulose nanofibrils (CNF)

- Most abundant biopolymer
- High tensile strength
- Reactive surface for functionalization
- 10 to 50 nm diameter, length can be up to a few micrometers
- Hydrophilic nature
- Tunable properties

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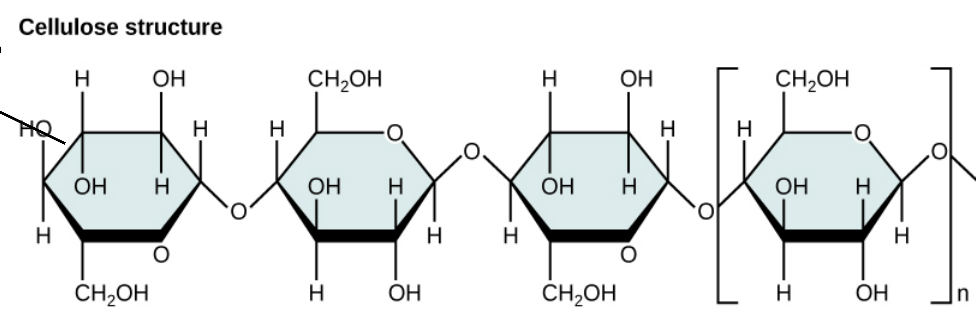
Glucose units



# Research Objectives

1. Effects of CNF on Cement hydration
2. Interaction between cement pore solution and CNFs
3. Effects of CNF on sulfate resistance
4. Effects of CNF on alkali-silica reaction (ASR)

# Experimental Setup

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- Fibril Diameter: 80-300 nm
- Fibril Length:100-500 µm
- Aspect Ratio: 800-1000 L/D
- DCNF was 34% solid in liquid form and LCNF was 29% solid in liquid form.

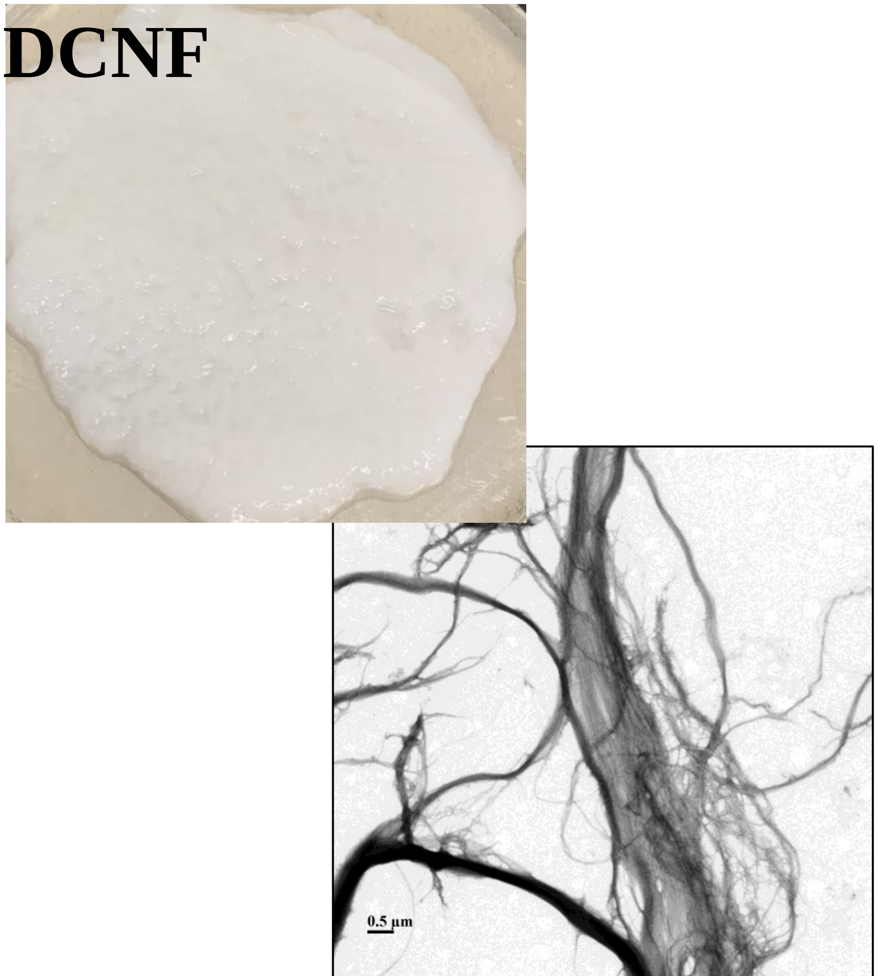
PERFORMANCE BioFilaments

| Cellulose type | Cellulose Doses (% of cement weight) | Binder |
|---|---|---|
| **Control** | 0% | Type I cement |
| **L-CNF** | 0.05% | |
| | 0.1% | |
| | 0.3% | |
| **D-CNF** | 0.05% | |
| | 0.1% | |
| | 0.3% | |

- **LCNF (Lignocellulose nanofibrils)** – made from unbleached (contains lignin) wood without any pre-treatment
- **DCNF (Delignified cellulose nanofibrils)** – made from bleached (i.e., delignified) wood pulp

# Cellulose Nanofibers






Cellulose nanofibers from bleached wood pulp (DCNF)


Cellulose nanofibers from unbleached wood pulp (LCNF)

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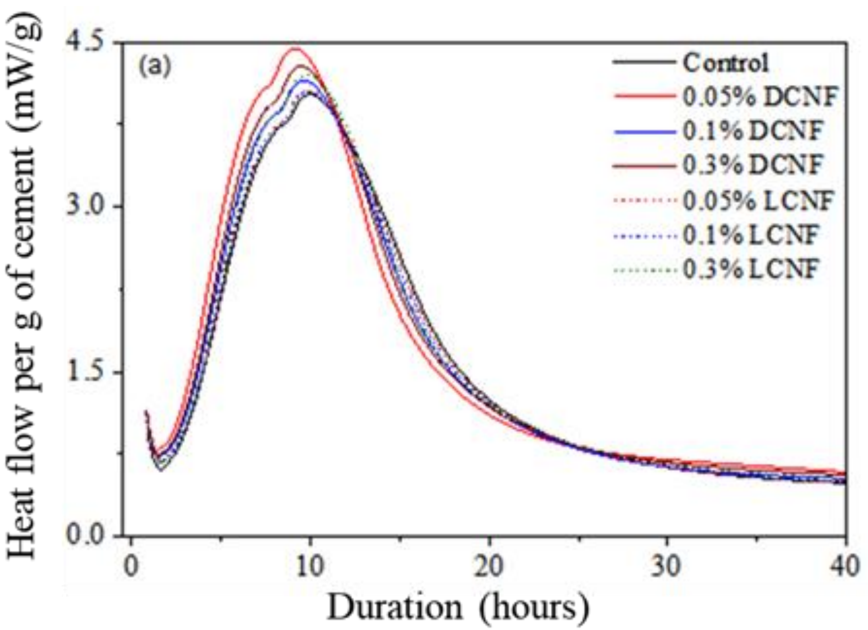
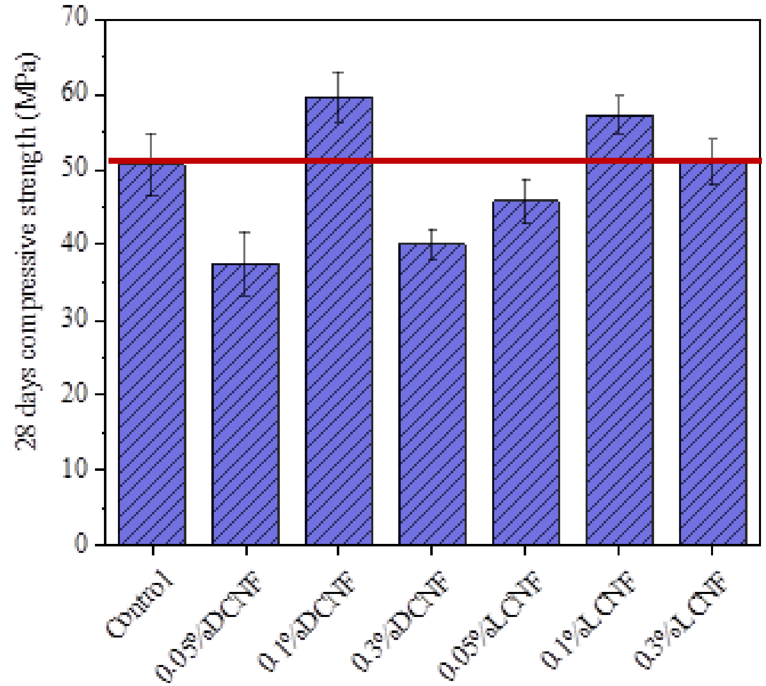
# Effects of CNF on Cement Hydration and Compressive Strengths

# Before Exposure Parameters




Effects of CNF on hydration




Effects of CNF on strength

**Takeaway:**

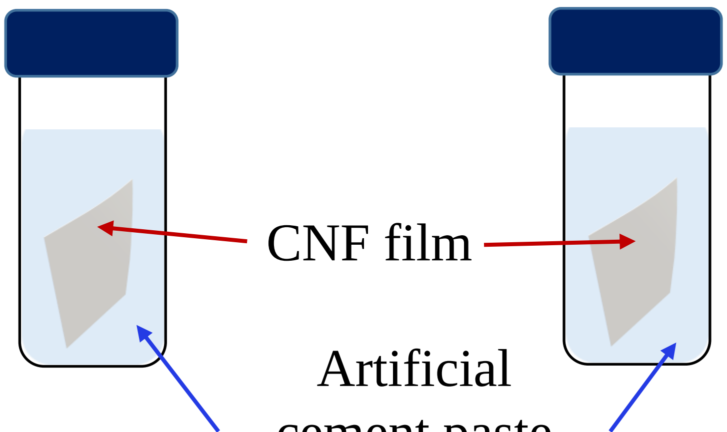
(i) Addition of CNF does not significantly affect the early age hydration reaction

(ii) 0.1% CNF dosages slightly improved 28-days compressive strength

# Interactions between Cement Pore Solution and CNFs

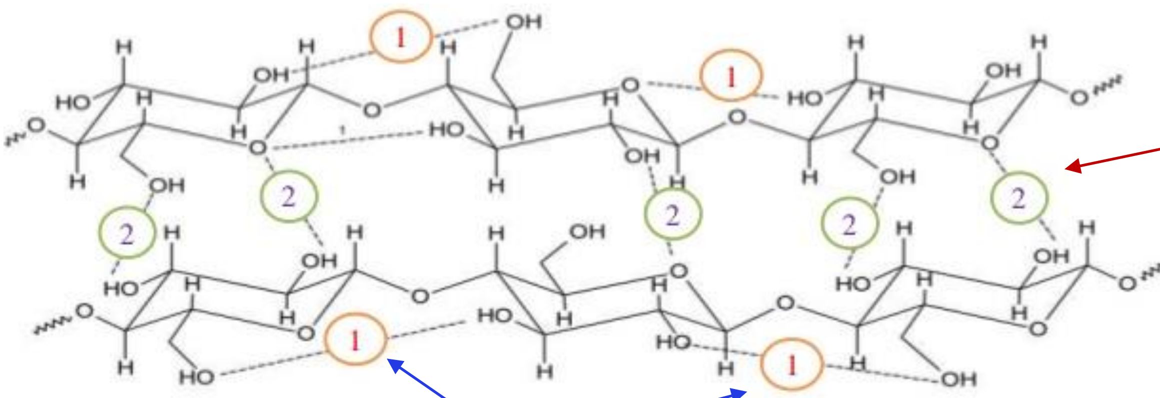
# Interaction between CNF & pore solution

- 28 days artificial pore solution (APS) of cement
- Chemical composition of APS: $Ca(OH)_2$, $Na_2SO_4$, NaCl, NaOH, KOH, $Al_2O_3$
- Curing conditions :
  - Regular curing : $23^0C$
  - Temperature curing : $70^0C$




- Pore solution chemistry was monitored using (Inductively coupled plasma - optical emission spectrometry (ICP OES)
- Cellulose film was analyzed using Fourier-transform infrared spectroscopy (FTIR)

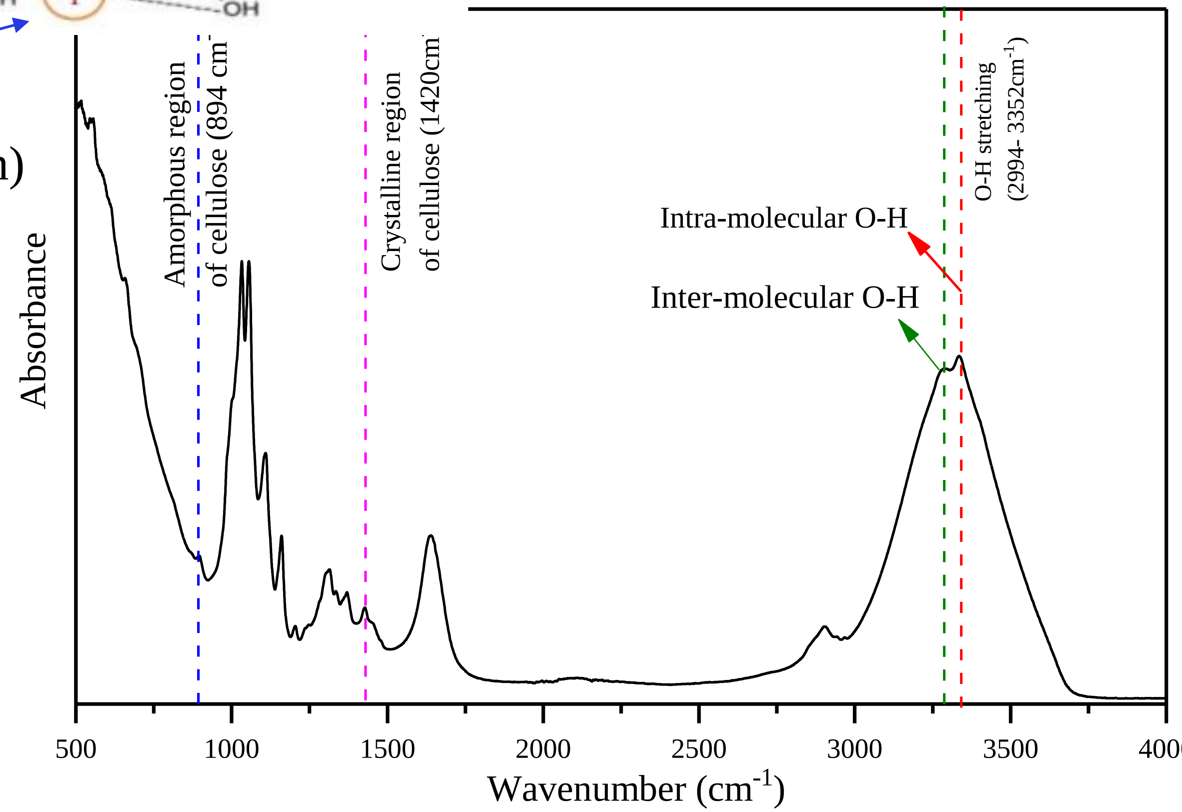
# Effects of Pore Solution on CNF



**Inter** OH Bond
(between two cellulose chains)

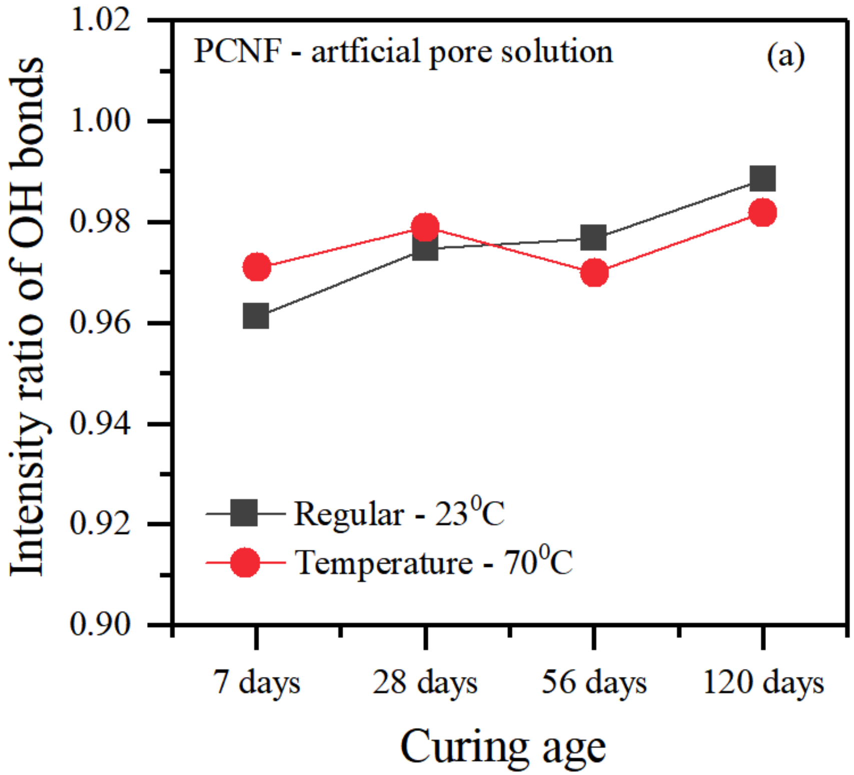
**Intra** OH Bond
(within a cellulose chain)

➢ Increase in intra OH bond indicates breaking of cellulose chain



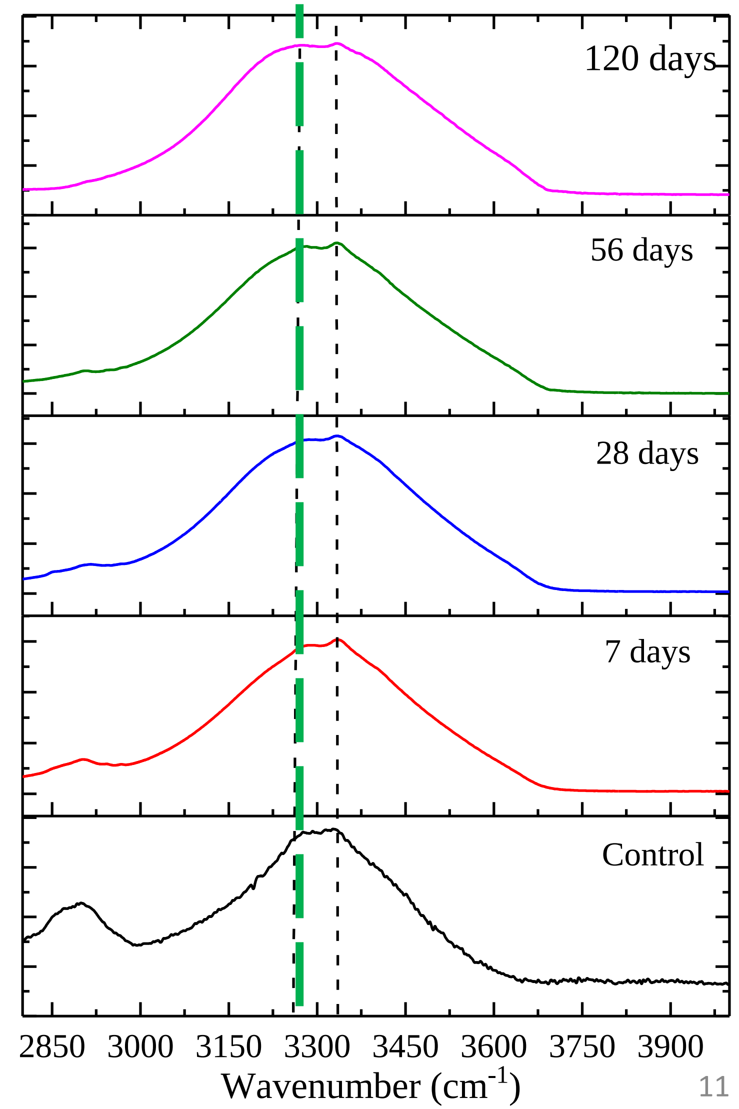
# Effects of Pore Solution on CNFs



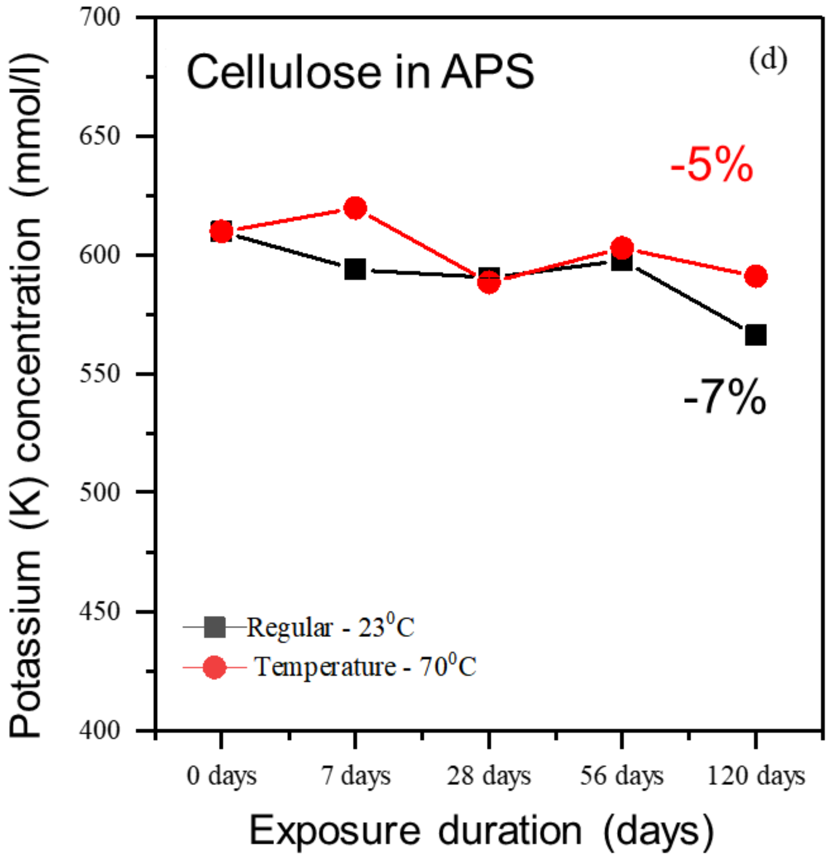


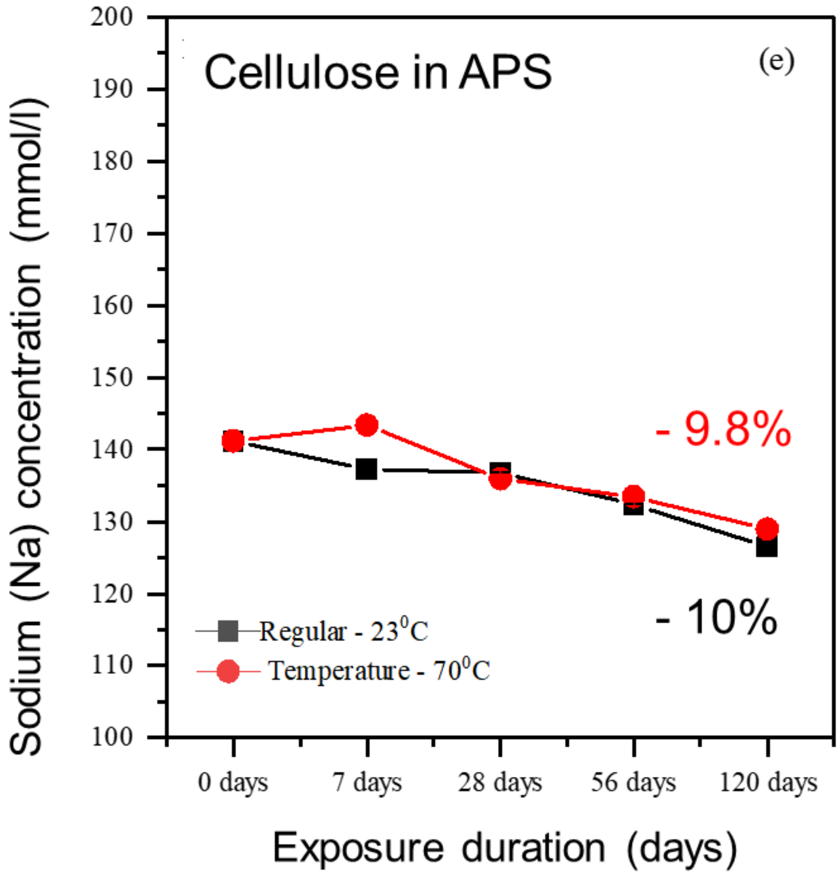

$$\text{Intensity ratio} = \frac{\text{Intensity of inter O–H}}{\text{Intensity of intra O–H}}$$

➢ Transformation of cellulose from amorphous phase → crystalline phase



# Effects of CNF on pore solution




- No other secondary phase precipitation was observed using X-ray diffraction

# Resistance to Sulfate Attack

# Sulfate attack in concrete: Cause and Significance

## Mechanism

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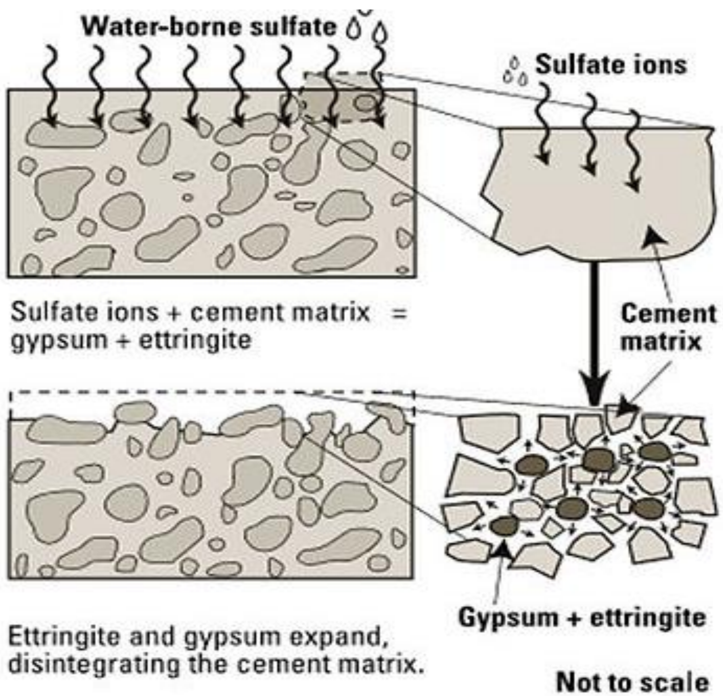


- **Current Practice:** Use of specialty cement (i.e., Type V cement)

## Appearance


*Concrete exposed to sulfate rich soil*

*Concrete exposed to sulfate rich water*

# Experimental plan for sulfate attack

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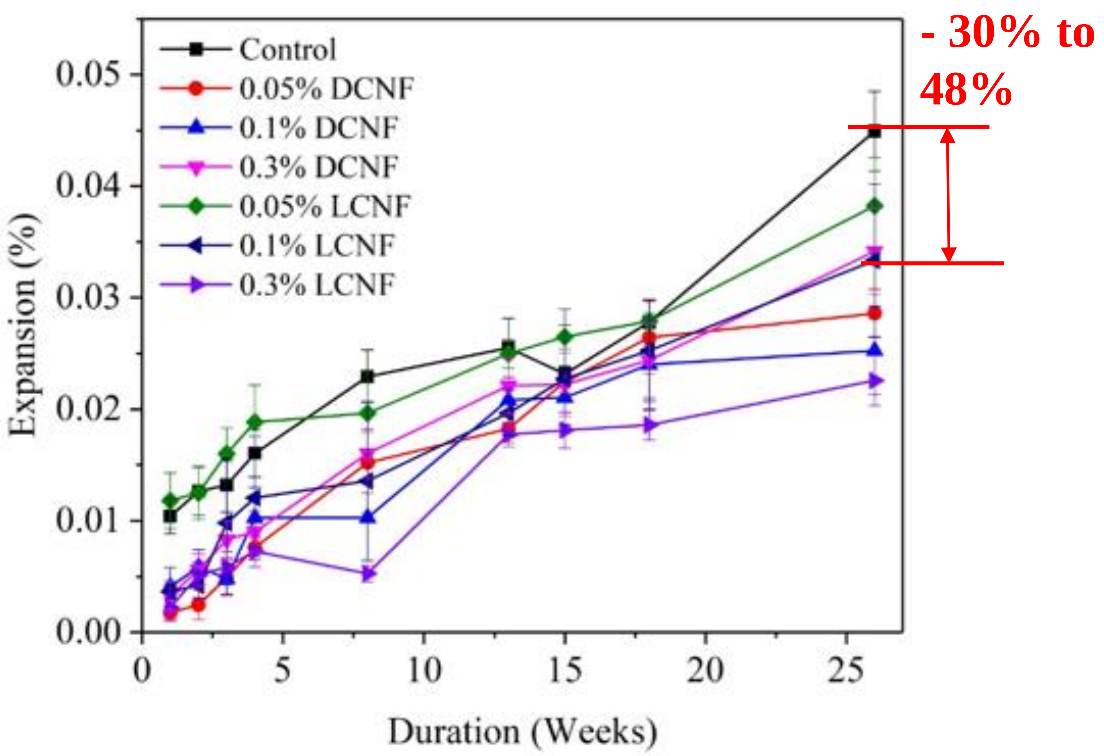
- ❑ Length change (**ASTM C 1012 standard**)
  - ❑ 5% $Na_2SO_4$
- ❑ Strength variation
  - ❑ Compressive strength on paste samples (28 days, 28+15, 28+1month, 28+3months, 28+6 months)
- ❑ Microstructure
  - ❑ TGA, XRD on paste samples (28 days, 28+15, 28+1month, 28+3months, 28+6 months)

Mortar bars for expansion measurement

Mortar cubes for strength measurement

# Samples exposed to $Na_2SO_4$ solution

## Length Change




| Sample ID | Expansion reduction (%) w.r.t control batch after 6 months in $Na_2SO_4$ |
|---|---|
| DCNF 0.05% | 46.67 |
| DCNF 0.10% | 47.88 |
| DCNF 0.30% | 18.38 |
| LCNF 0.05% | 25.25 |
| LCNF 0.10% | 33.73 |
| LCNF 0.30% | 50.9 |

**Takeaway:** Sample expansion was reduced by 30 to 50% due to the addition 0.1% CNF

# Samples exposed to $Na_2SO_4$ solution

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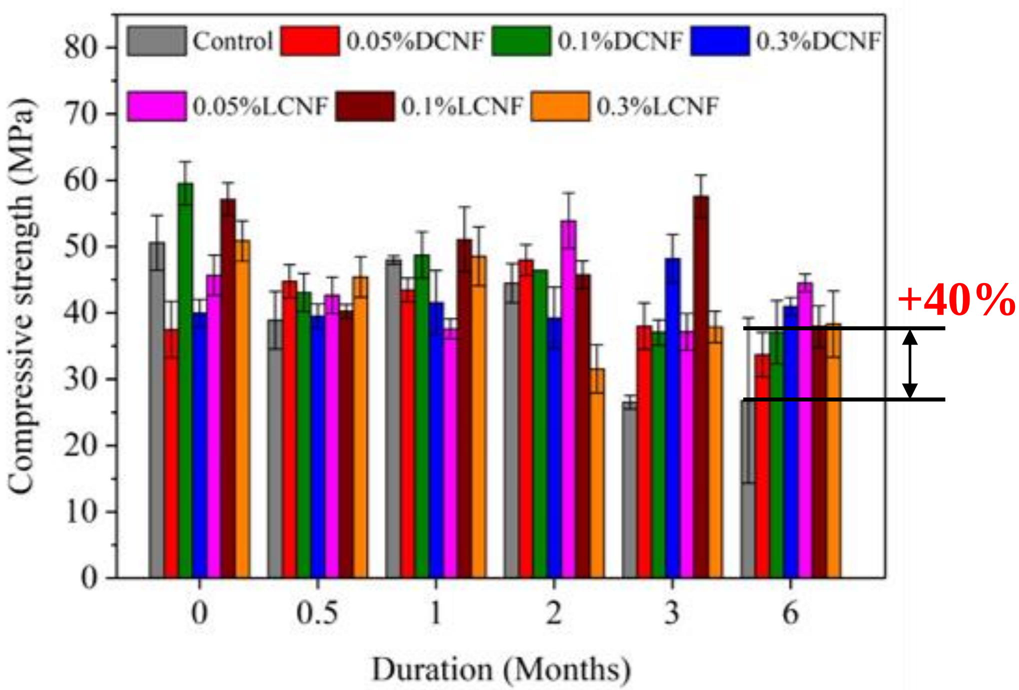
## Compressive strength




| Sample ID | Change in compressive strength after 6 months exposure | |
|---|---|---|
| | w.r.t. control | w.r.t. before exposure strength |
| **Control** | **----** | **− 47.01** |
| DCNF 0.05% | + 25.68 | − 10.11 |
| **DCNF 0.10%** | **+ 38.39** | **− 37.66** |
| DCNF 0.30% | + 52.83 | + 2.58 |
| LCNF 0.05% | + 66.08 | + 2.55 |
| **LCNF 0.10%** | **+ 41.46** | **− 33.62** |
| LCNF 0.30% | + 42.91 | − 24.65 |

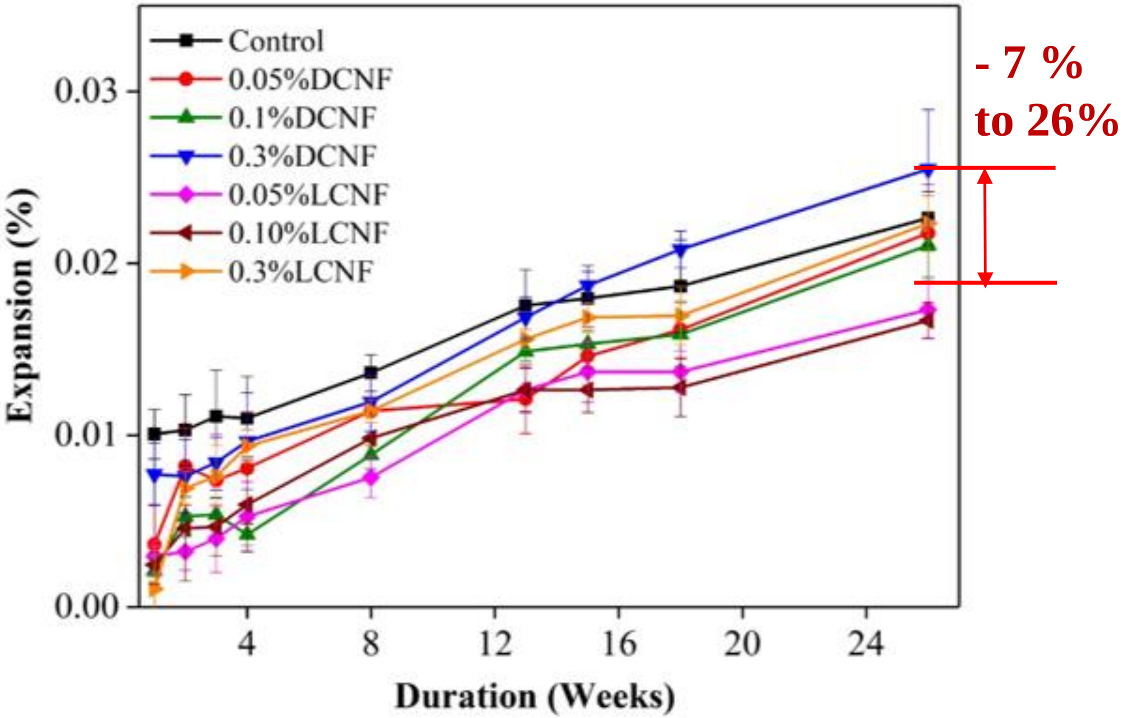
**Takeaway:**

(i)There was no specific trend with dosage

(i)After 6 months exposure, control batch (without CNF) had the lowest strength

# Samples exposed to $MgSO_4$ solution

## Length Change



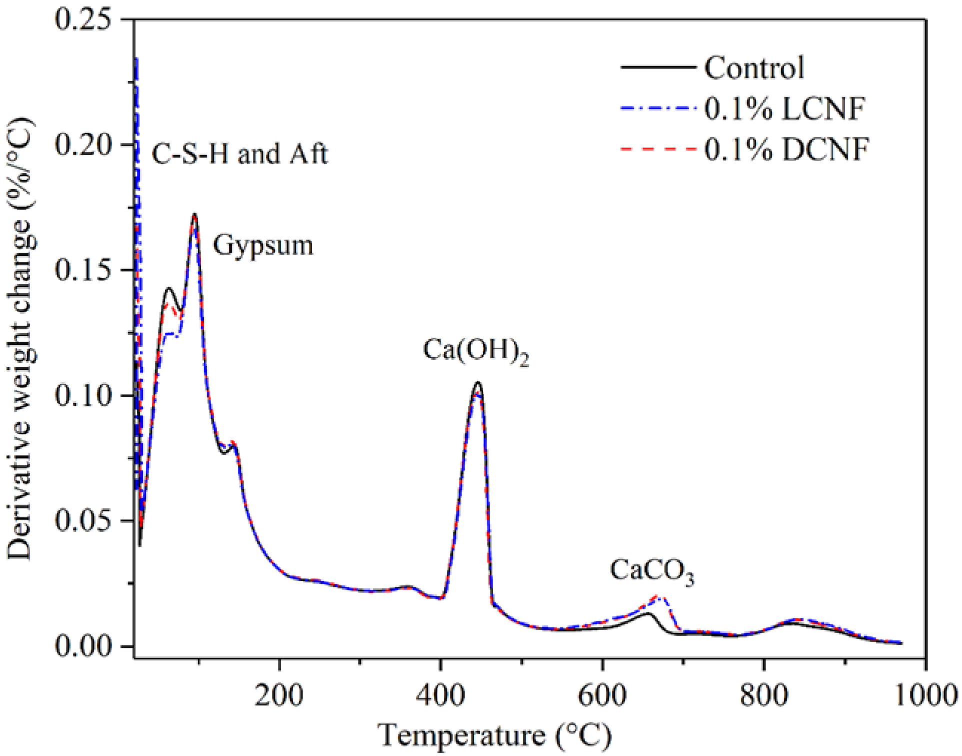

| Sample ID | Expansion reduction (%) w.r.t control batch after 6 months in $Na_2SO_4$ |
|---|---|
| DCNF 0.05% | -3.87 |
| **DCNF 0.10%** | **-6.97** |
| DCNF 0.30% | + 12.66 |
| LCNF 0.05% | -23.51 |
| **LCNF 0.10%** | **-26.36** |
| LCNF 0.30% | -1.39 |

**Takeaway:** Sample expansion was reduced by 7 to 26% due to the addition 0.1% CNF

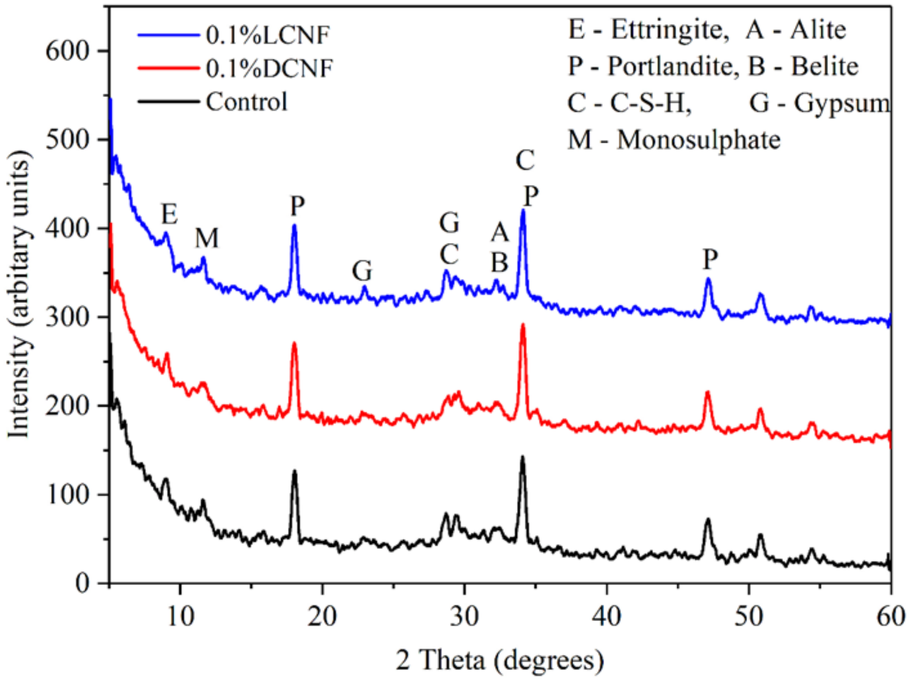
# Mechanisms preventing sulfate damage

## Microstructure

*Thermogravimetric analysis (TGA)*




*X-ray Diffraction (XRD)*

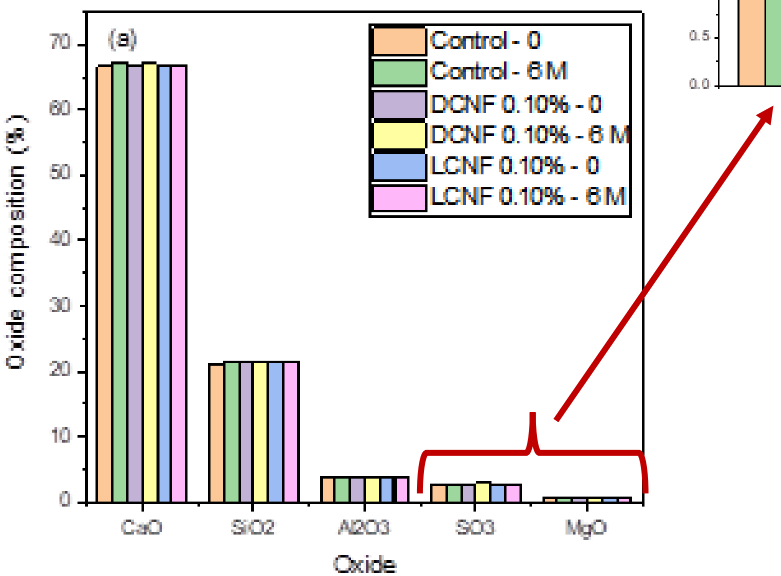


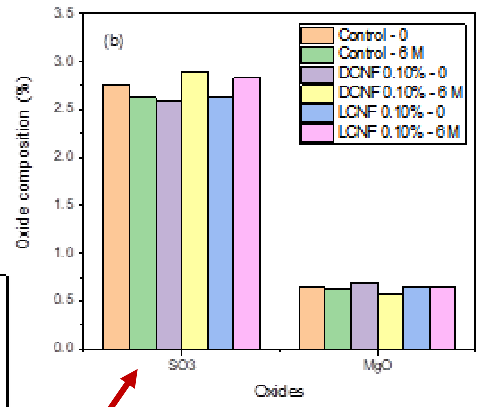

**Takeaway:**
The addition of CNF reduced gypsum and ettringite formations.

# Mechanisms preventing sulfate damage

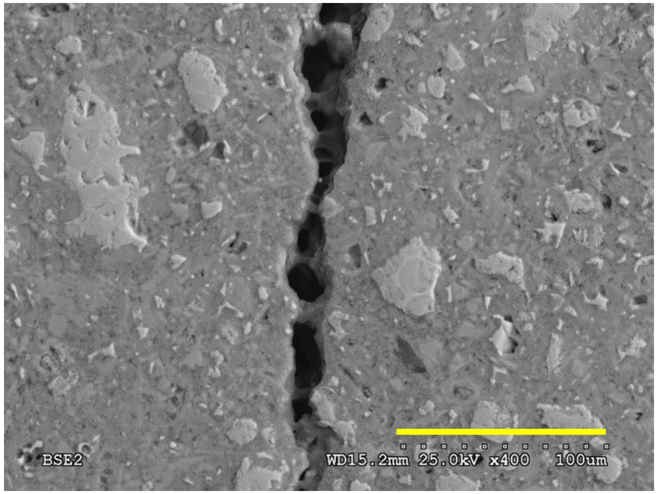
## Microstructure

*X-Ray Fluorescence (XRF)*




*Scanning electron microscopy (SEM)*

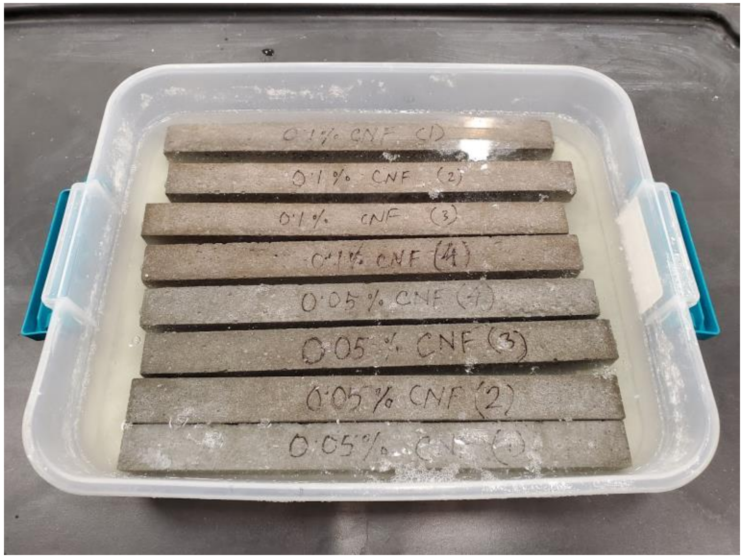



**Takeaway:** The addition of CNF improves resistance to sulfate damage by (i) reducing gypsum and ettringite formations, and (ii) bridging the cracks.

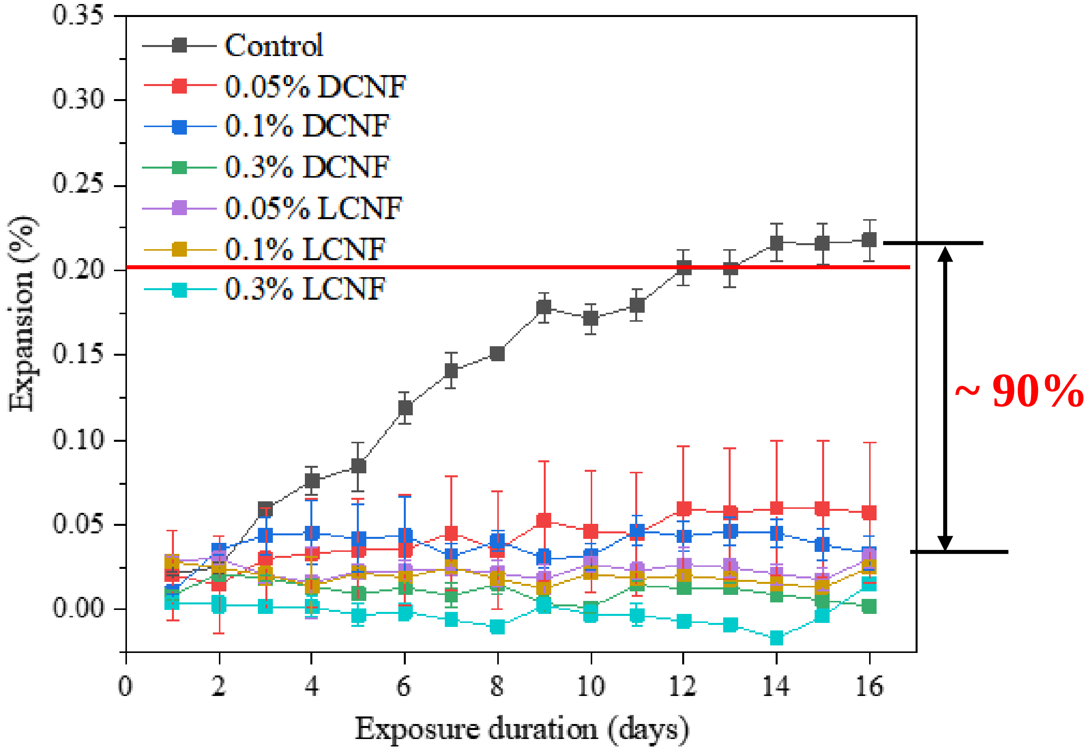
# Resistance to
# Alkali Silica Reaction (ASR)

# ASR Susceptibility test

- Test method: ASTM C 1260
- Water to cement ratio = 0.5
- Aggregate type: sodium borosilicate
- Bar immersed in 0.1N NaOH solution at 80$^{O}$C
- Measurements taken at 24 hours interval up to 16 days

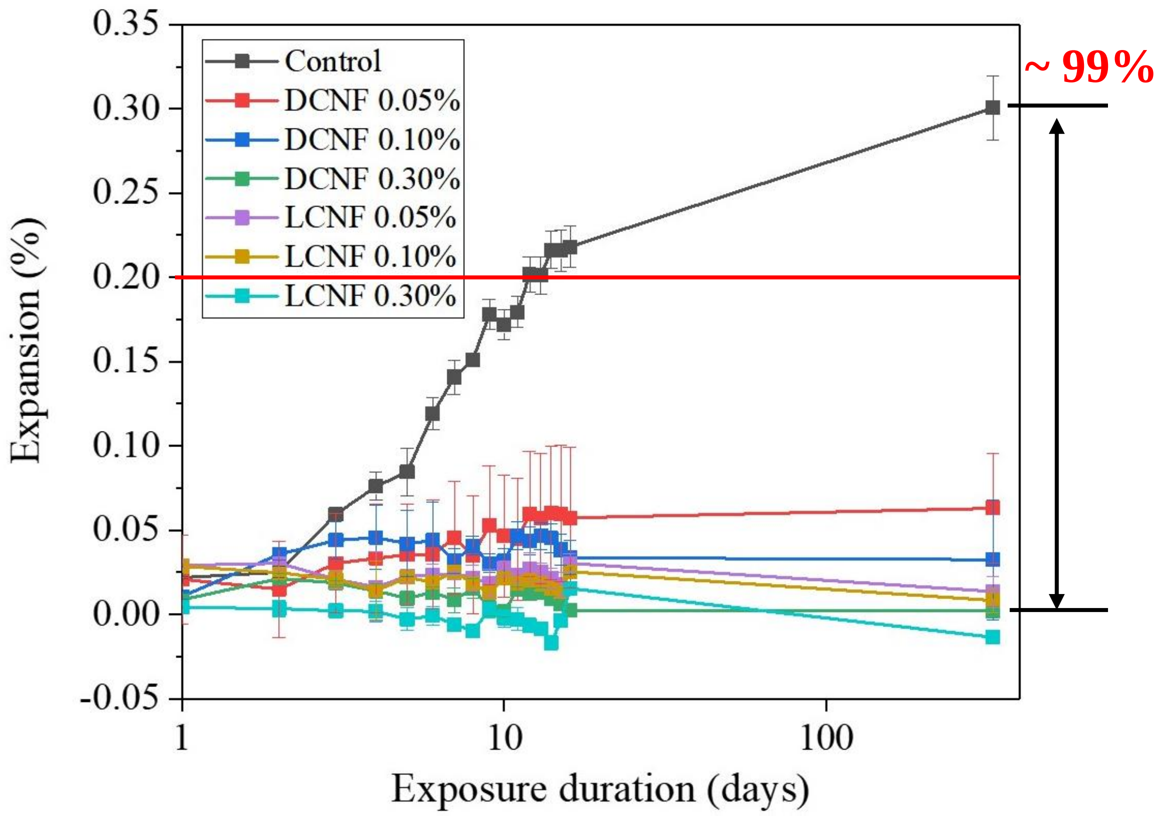
# Effects of CNF on Alkali-Silica Reaction




| Sample ID | Expansion reduction (%) w.r.t control batch after ASR reaction |
|---|---|
| DCNF 0.05% | 73.71 |
| DCNF 0.10% | 84.59 |
| DCNF 0.30% | 98.89 |
| LCNF 0.05% | 86.06 |
| LCNF 0.10% | 88.38 |
| LCNF 0.30% | 92.90 |

**Takeaway:** Sample expansion was reduced by 80 to 90% due to the addition 0.1% CNF

# Effects of CNF on Alkali-Silica Reaction




| Sample ID | Expansion reduction (%) w.r.t control batch after ASR reaction |
|---|---|
| DCNF 0.05% | 79.0 |
| DCNF 0.10% | 89.2 |
| DCNF 0.30% | 99.3 |
| LCNF 0.05% | 95.5 |
| LCNF 0.10% | 97.2 |
| LCNF 0.30% | 104.5 |

**Takeaway:** Sample expansion was reduced by 99% due to the addition of 0.1% CNF

# Resistance to Atmospheric Carbonation

# Atmospheric Carbonation: Cause and Significance

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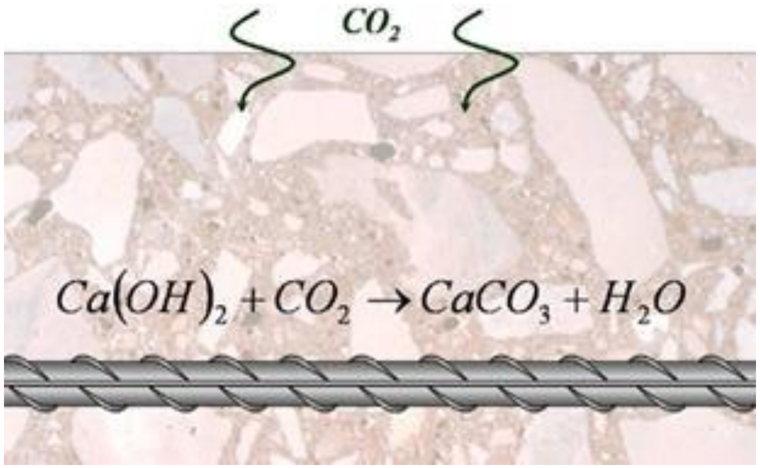
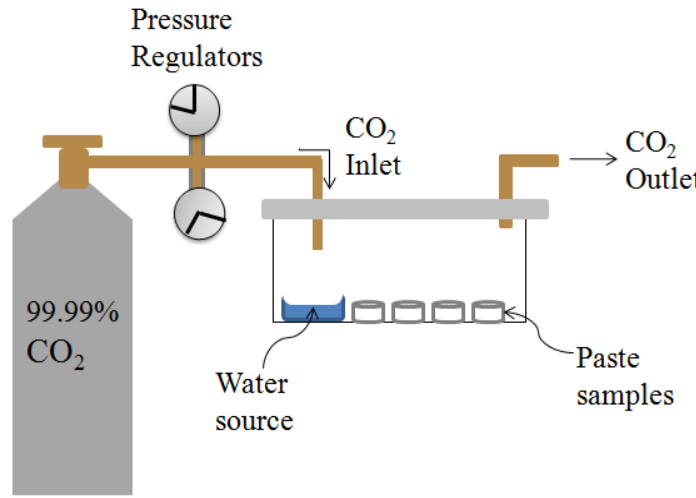
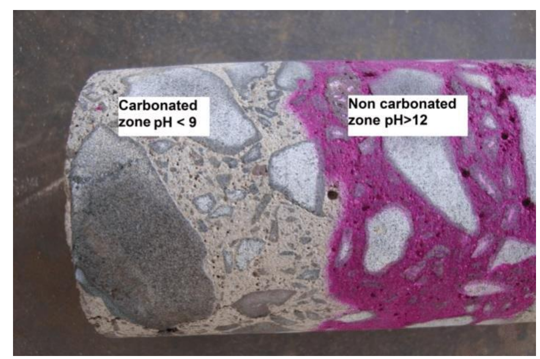



The carbonation reaction reduces the pH of the pore solution to less than 9, which leads to the destruction of the passive oxide layer protecting the steel bars from corrosion




Carbonation setup

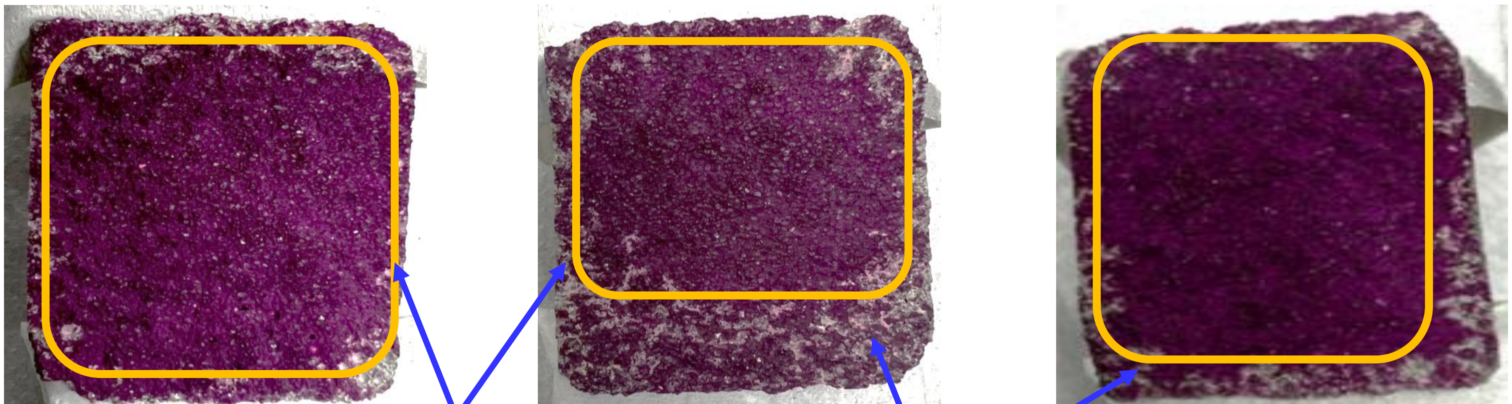



Phenolphthalein indicator test

# Effects of CNF on Atmospheric Carbonation

## 28 days carbonation

Control | 0.3% DCNF | 0.3% LCNF



Non-Carbonated zone

Carbonated zone

**Takeaway:** (i) Effects of CNF on atmospheric carbonation resistance of mortar samples were inconclusive. (ii) For certain cases, the addition of CNF appeared to increase the carbonation.

# Conclusions

- The addition of CNF significantly (~ 50%) reduced sulfate damage in mortars.
- For most of the durability tests, LCNF containing samples performed slightly better (~ 10%) than the DCNF
- Due to the alkaline hydrolysis, the degree of crystallinity of CNF increases with time when exposed artificial pore solution
- The addition of CNF reduced the expansion of mortar samples due to the ASR by more than 90%.
- For durability performance enhancement, 0.1% dosage of CNF was found to be optimum.
- Additional studies are required to understand the effects of CNF on carbonation. This can be helpful in increasing carbon sequestration in concrete.

P$^3$Nano

# Thank you!

warda.ashraf@uta.edu