The Role of Chemistry in High Performance Cement via CNC Addition

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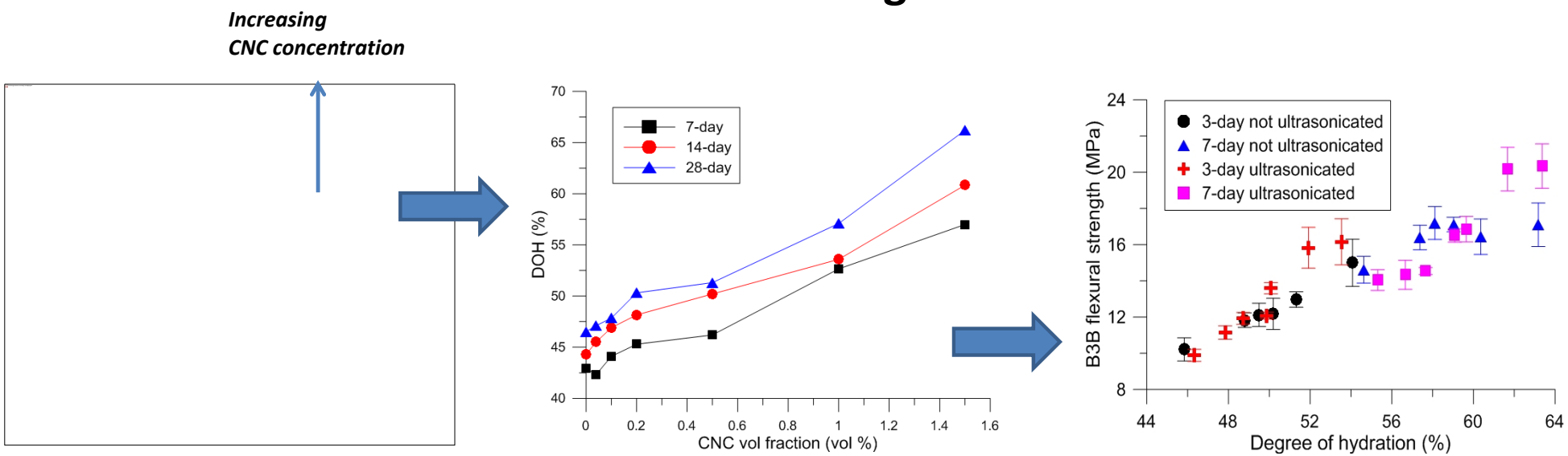
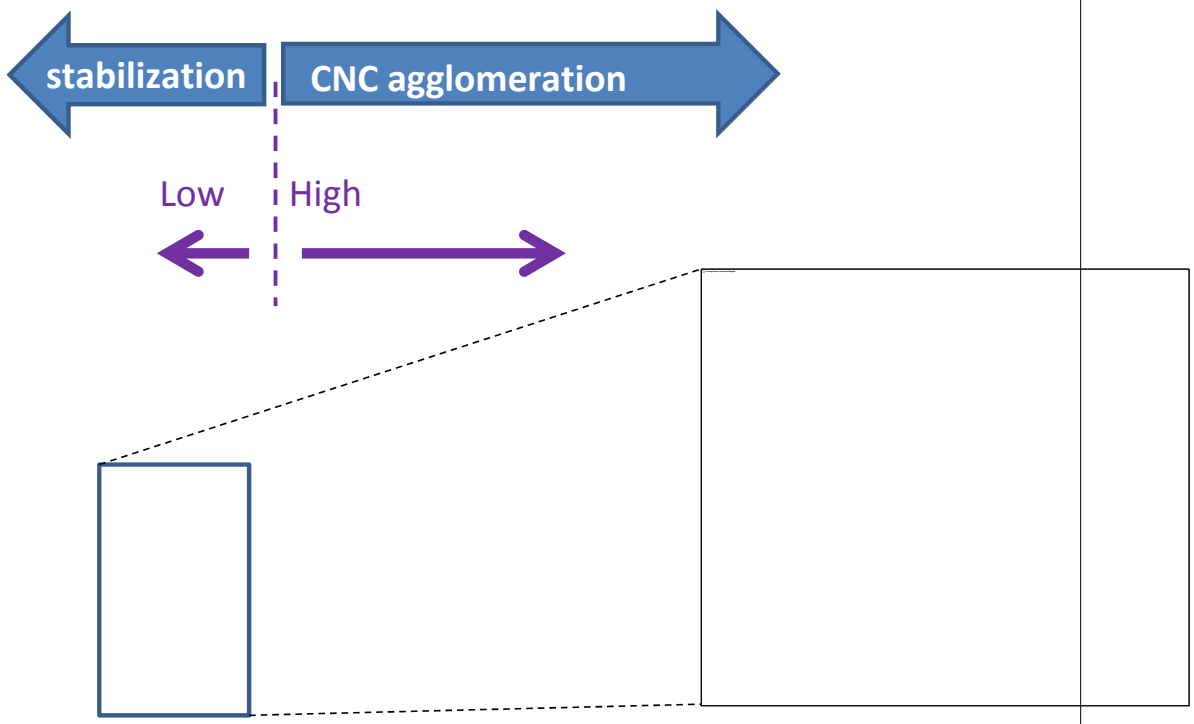
Degree of Hydration (DOH) is increased by CNC which leads to higher flexural strength



- Heat release and therefore Degree of Hydration (DOH) is increased with CNC
- CNC induces a delay in onset of cure
- Flexural strength scales with hydration (as expected)

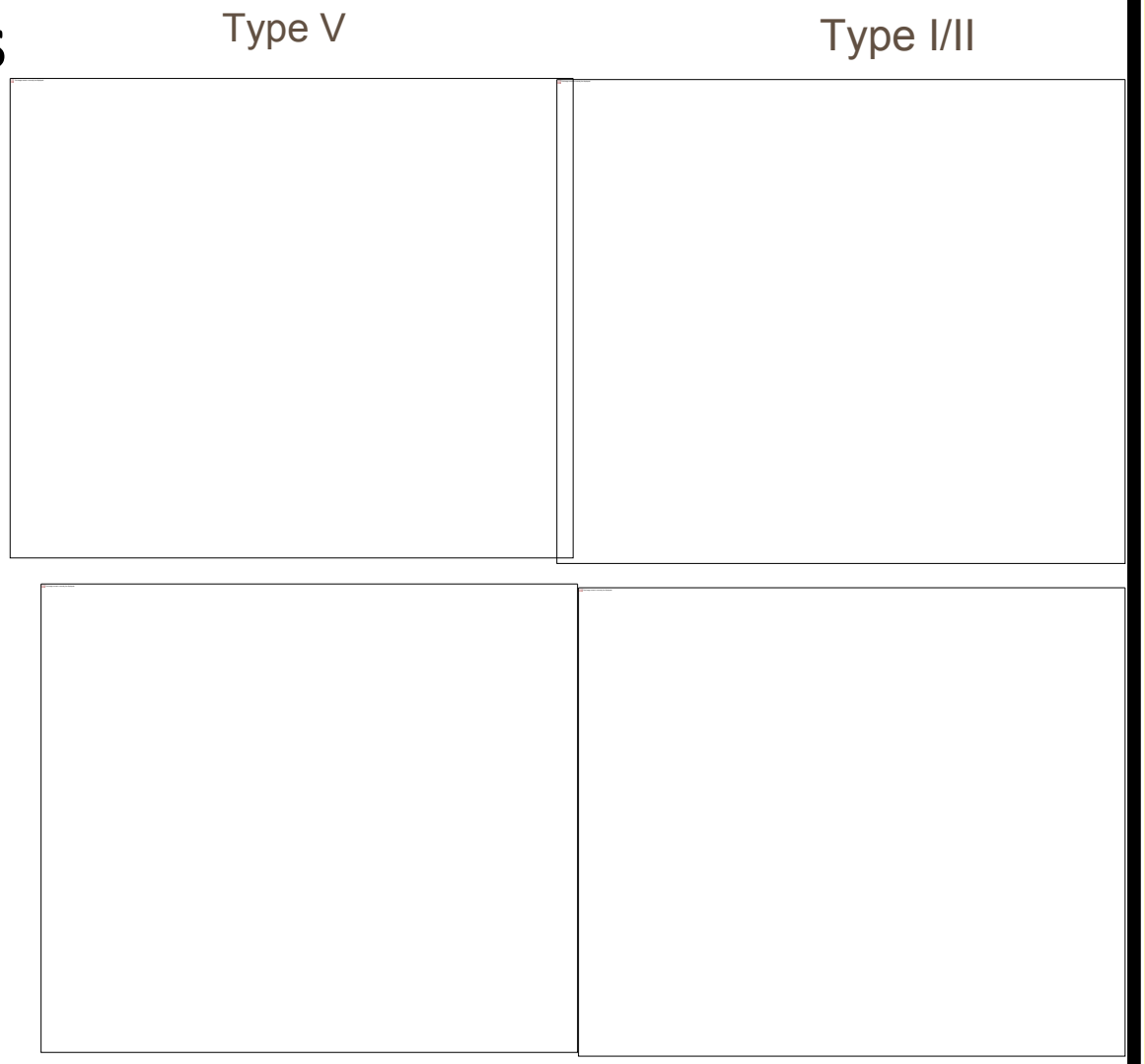
Yield stress shows colloidal stabilization at low concentration



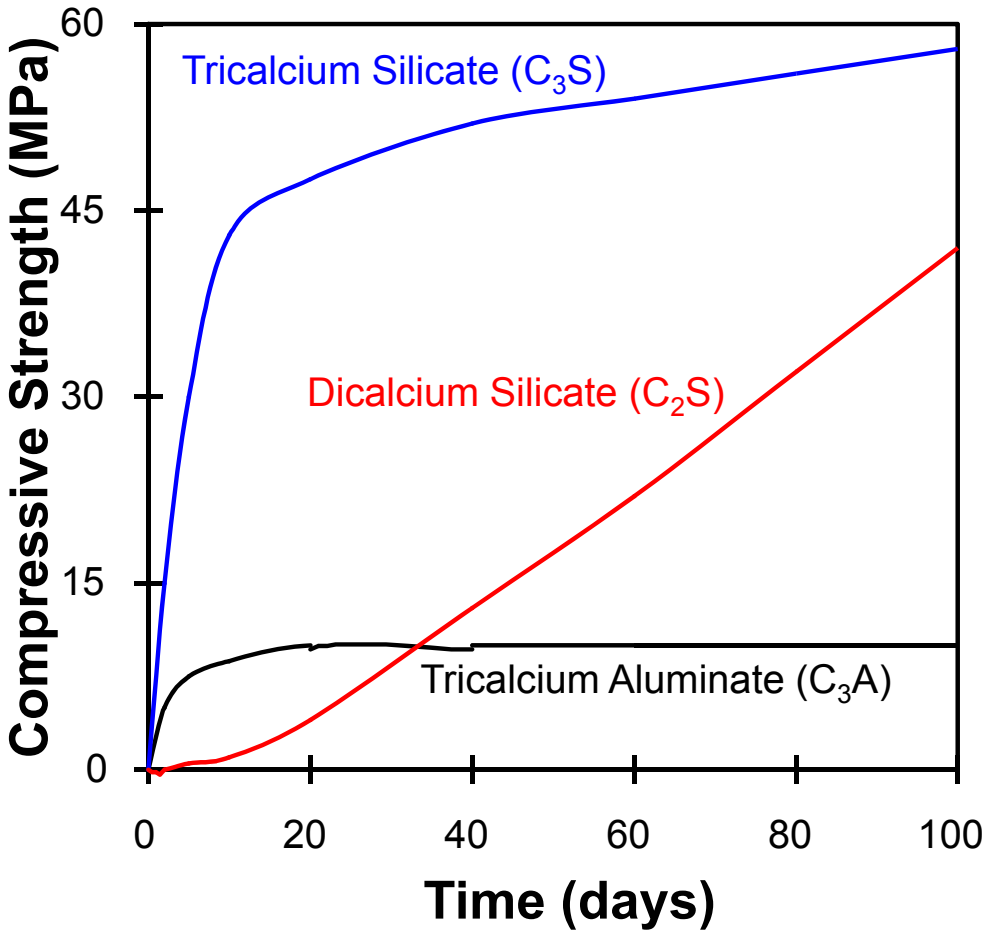
- CNC addition leads to yield stress reduction
  - Indicates colloidal stabilization
- At high content yield is increased
  - Aggregation?
- Workability enhancers called “Plasticizers” or “Water Reducers” are added commercially to obtain same effect

Unfortunately it appears that chemistry of cement is important – CNC % Type I/II vs V

- Type I/II has less heat release (DOH) increase than Type V with CNC
- Type I/II also has a decreased set delay
- Increase in 2° Aluminate / Sulfate Depletion peak (Ettringite) for Type I/II



How do Type I/II and Type V differ?



- C_3A Reacts Instantaneously
  Good for early strength but not significant for LT
- C_3S reacts to give early strength
- C_2S reacts to give long-term strength

Type I has 7% C_3A while Type V has very little

TOCNC may have a higher degree of cure than sulfate CNC!

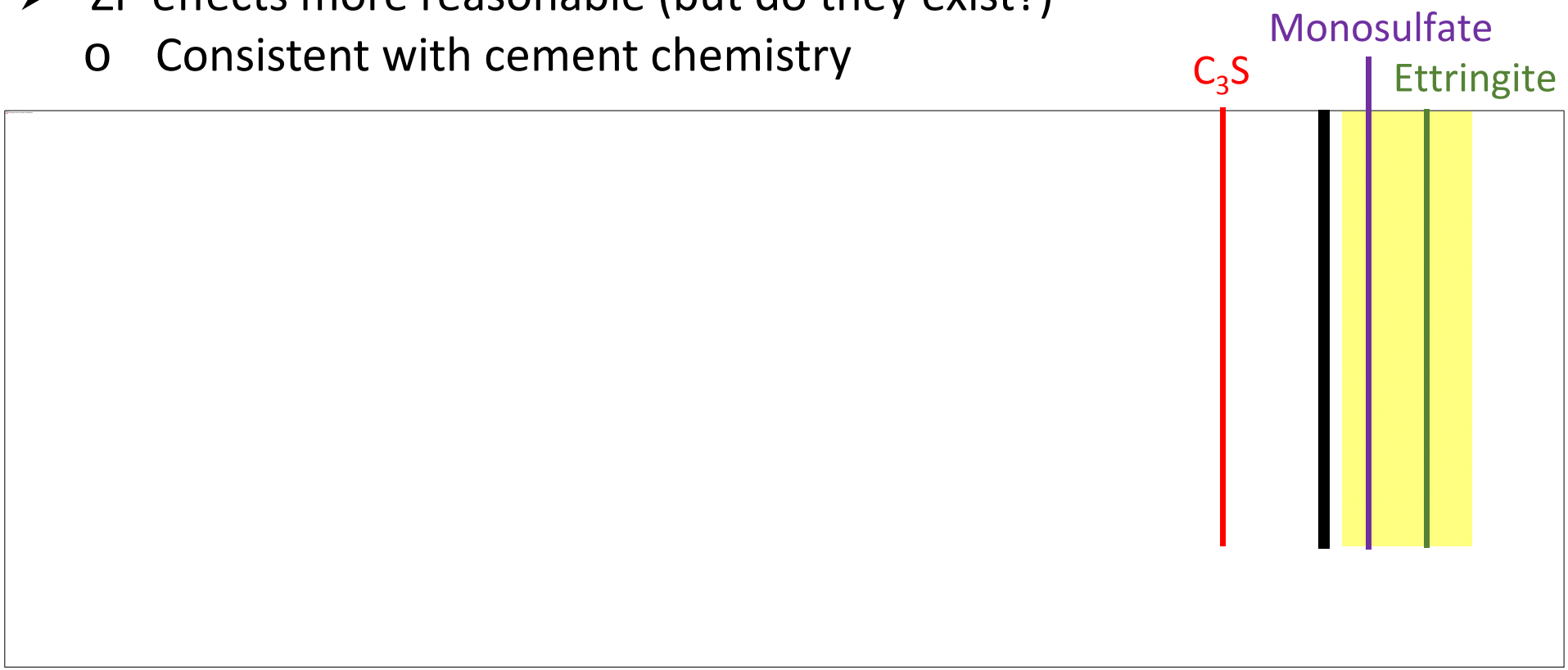
CNC Content (%)	Heat Release (W/g of cement)
0% CNC/CNF	287.44
0.2% CNC-117	284.03
0.5% CNC-117	289.19
0.2% CNC-120 (TEMPO)	287.45
0.5% CNC-120 (TEMPO)	**292.97**

TOCNC has higher degree of cure (DOC) over sulfate CNC at similar dosages at 7 days.

(Unfortunately, the increase is insignificant (currently) due to low test number)

What is going on?

- Reason for length dependence – No earthly clue!
- ZP effects more reasonable (but do they exist?)
  - Consistent with cement chemistry



Issue #1 - Now about that delay

Delay of different 0.2% CNCs

Delay of Glucose on Type V

- Different CNCs show different delays
- Different lengths or charge – no trend found
- Contaminant?

While "sugar" contamination in CNC is low, it may still affect cement!

Saccharide Impurity (wgt%)	Sugar concentration per cement at _____vol% CNC			
	0.20%	0.50%	1.00%	1.50%
0.0798%	0.000671%	0.001677%	0.003354%	0.005032%
0.0008%	0.000007%	0.000018%	0.000036%	0.000054%
0.0710%	0.001821%	0.004551%	0.009103%	0.013654%
0.0256%	0.000224%	0.000561%	0.001122%	0.001683%
0.1200%	0.000985%	0.002462%	0.004923%	0.007385%
0.0078%	0.000060%	0.000150%	0.000301%	0.000451%
0.0689%	0.000955%	0.002387%	0.004775%	0.007162%
0.0743%	0.001030%	0.002574%	0.005149%	0.007723%

“Sugar” is present in CNCs, but is larger polysaccharides

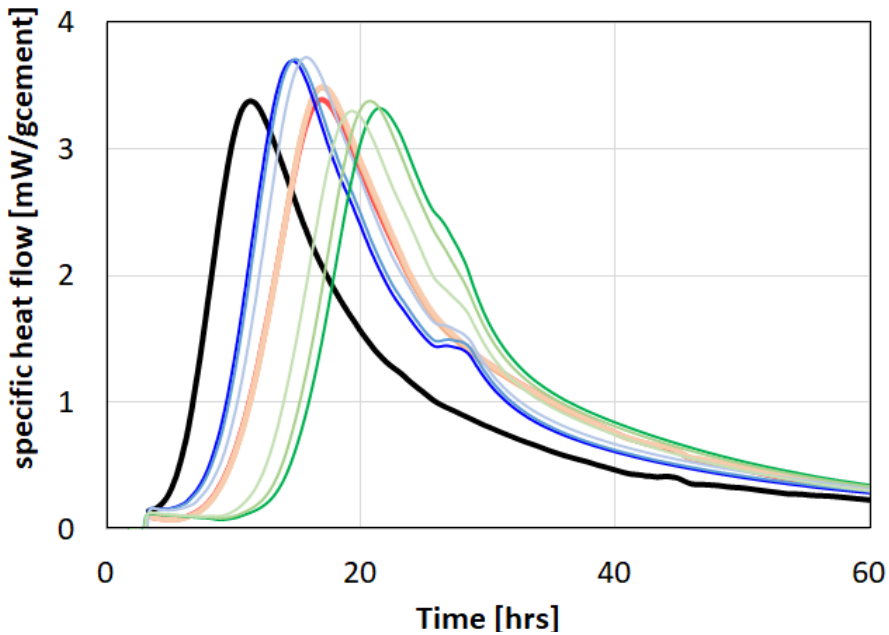
- CNC is separated from media by high pressure nanofiltration
  - 300 kD chosen to make sure to capture all contaimants
- No glucose detected (glucose monitor)
- Very low levels of sugars detected by typical reducing-end tests
- HPLC and MALDI detect larger MW polysaccharides (cellobiose up to 1-3 kD)

So how can we quantify levels of polysaccharides?

- Anthrone test! – a non-specific measurement of polysaccharides that labels ring, not reducing end.
- Measure via UV-Vis
- With a few exceptions, uncorrelated with set delay of CNC.
- Some have other things (like organic acids)

Removal of polysaccharide did not change the delay by much

- Sonication/Filtration was used to remove polysaccharide



<u>Take-home message #1:</u> Washing to a conductivity end-point is not sufficient to remove the polysaccharides (they are larger and adsorb more strongly).

<u>Take-home message #2:</u> We have an easy method to test for polysaccharides (Anthrone)

<u>Take-home message #3:</u> Most CNCs are sufficiently clean for cement.

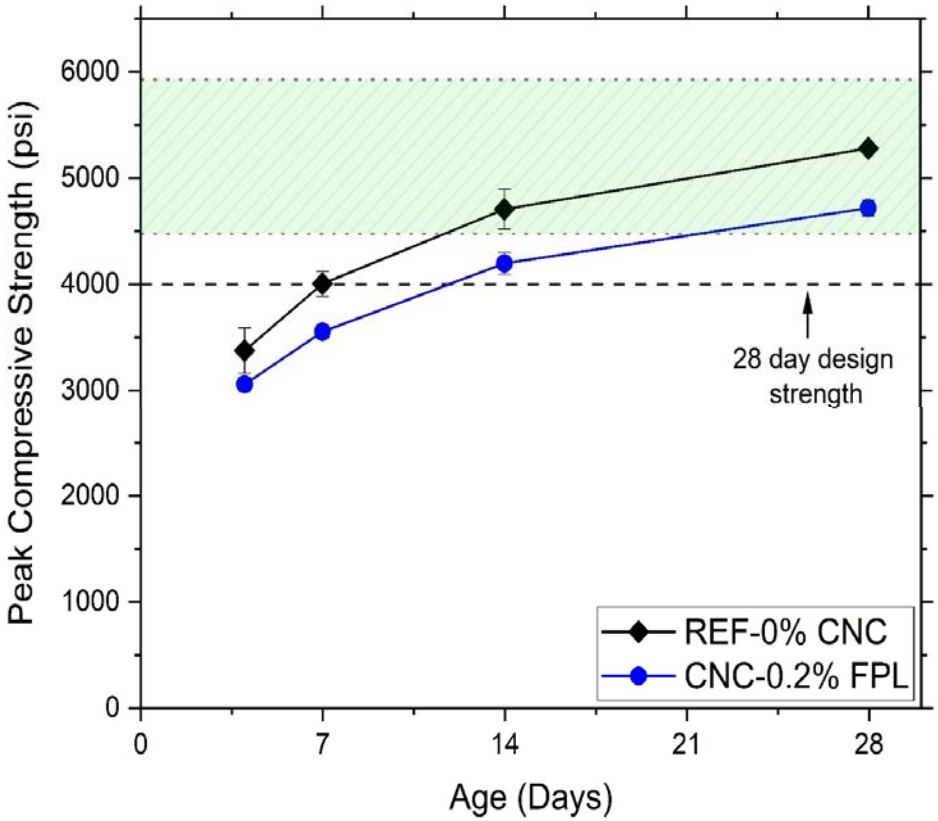
CNC-concrete works at even larger scale!

- A CNC-concrete parking lot was poured at the US Endowment in Greenville, South Carolina
- 60 cubic yards of CNC concrete were poured at 0.2% dosage (and 10 yards of standard concrete
- What we learned during the pour:
  - The CNC concrete behaved as well as standard concrete during placement
  - No apparent adverse effects when using heated water for batching CNC concrete
  - No apparent adverse effects on CNC concrete placement due to the cold weather

However, there was a decrease in strength not observed elsewhere

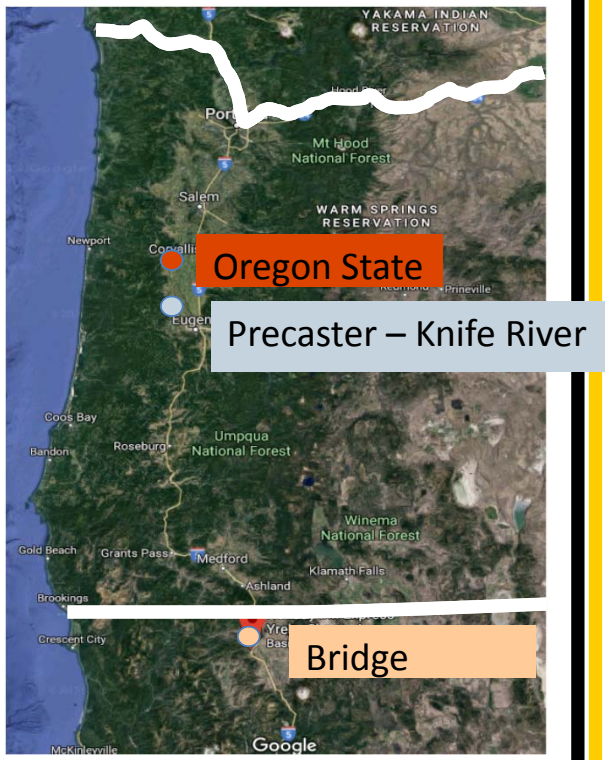
- CNC concrete met target 28-day design strength by 14 days (ie meets spec using actual mixes and contractors)
  - Green area is expected compressive strength based on a design strength of 4000 psi considering the standard deviation between each batched concrete truck
- However, compressive strength of CNC samples showed an 11% decrease at 28 days compared with the reference
  - Possible interaction with fly ash used in SC

Issue #3 – Regional variabilities in SCM can have an effect



Now for the real-world

- Locations in Siskiyou Co California are being examined for a CNC-cement enabled bridge
- Considerations include foundations (practical consideration)



However, turns out that the bridge will be precast

- Originally we were gearing up for ready mix concrete applications
- This is an important distinction:
  - Composition differs
  - Mixing/delivery differs

Precast

[redacted]

Readymix

Summary

- Strength in cement is increased and plasticization by addition of CNCs cement.
- Mechanism is thought to be short circuit diffusion that increases DOH
- Cement chemistry matters:
  - Type V shows larger strength and DOH benefit than Type I – likely due to aluminates
- CNC matters:
  - CNCs from different vendors show differences – maybe strength, maybe chemistry/charge
- Admixtures (WRAs, etc) matter and can have deleterious effects on flow/slump
- SCMs (flyash) matters and can have deleterious effects on strength.

Even if everything is perfect, need to balance CNC dosage to achieve desired strength, delay and workability

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Thank you

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