Temple University
College of Engineering

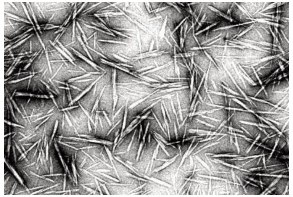
Application of Cellulose Nanomaterials in 3D Printed Low/Zero Clinker Cementitious Systems

Abdullah-Al Fahim, PhD Student, Temple University
Mehdi Khanzadeh, Associate Professor, Temple University

Motivation

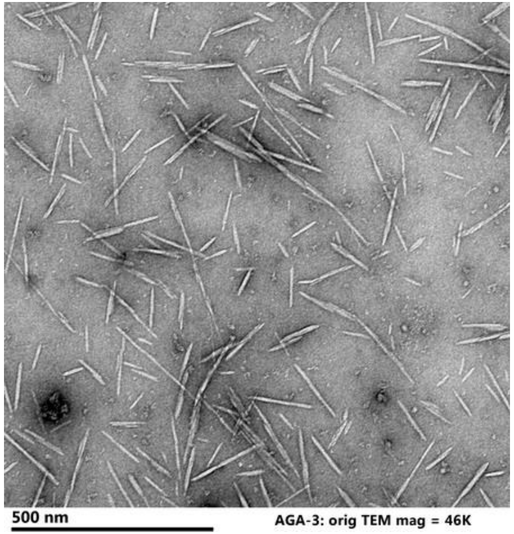
Temple University
College of Engineering

- 3D printed cementitious materials has been receiving increasing attention
- Challenges exist to deliver cost-effective and sustainable 3D printed cementitious mixtures
- Cellulose Nanomaterials are “green” nanoparticles that can improve the mechanical properties of cement-based materials
- **Application of CN-materials in low/zero clinker composites**

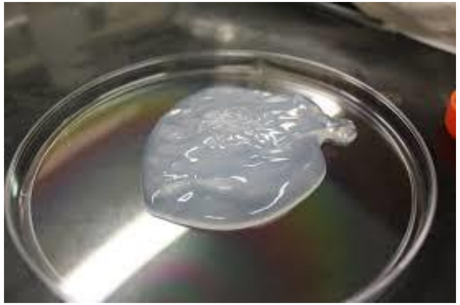


Cellulose Nanomaterials

- Cellulose nanocrystals (CNC) are the crystalline part of these polymers usually extracted from trees and plants.
- CNCs are typically 0.05 – 0.5 μm long and have a width of 3 – 5 nm.
- CNCs are renewable, biodegradable, sustainable, and present in high abundance in nature.

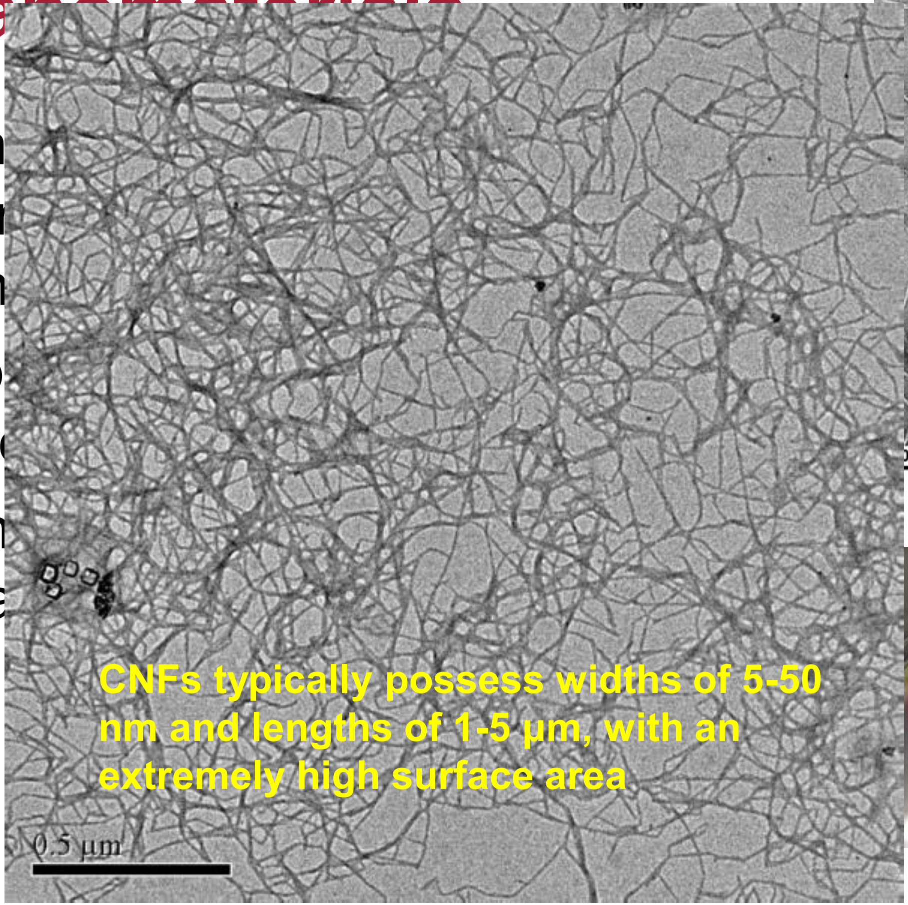


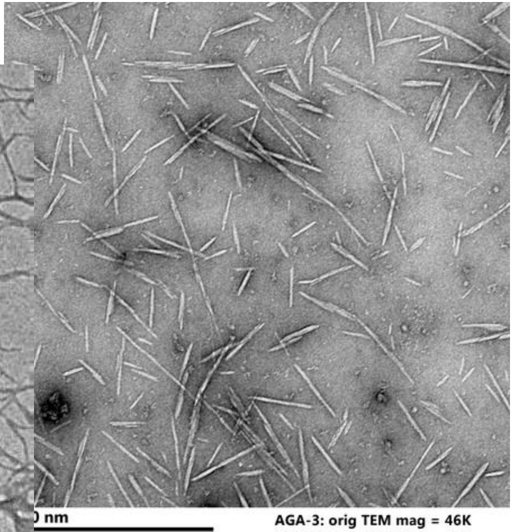
FPL



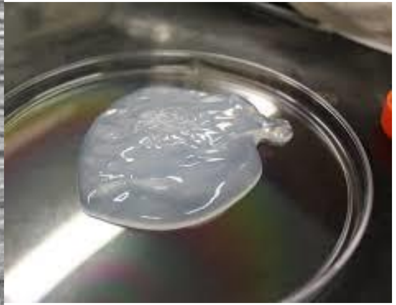
Cellulose Na

- Cellulose nan crystalline pa extracted fron
- CNCs are typ have a width
- CNCs are ren sustainable, a in nature.

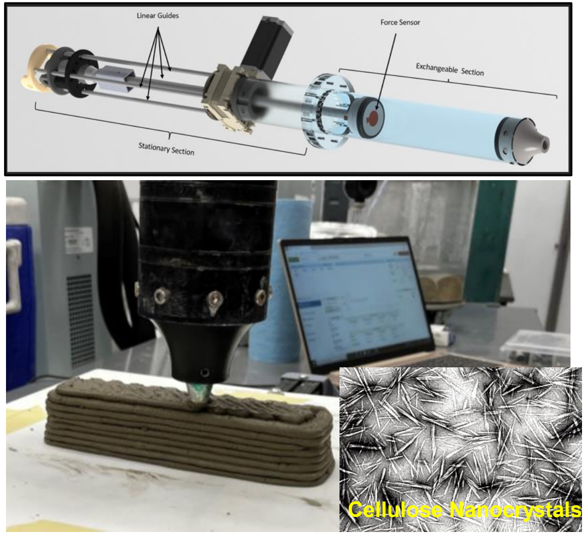




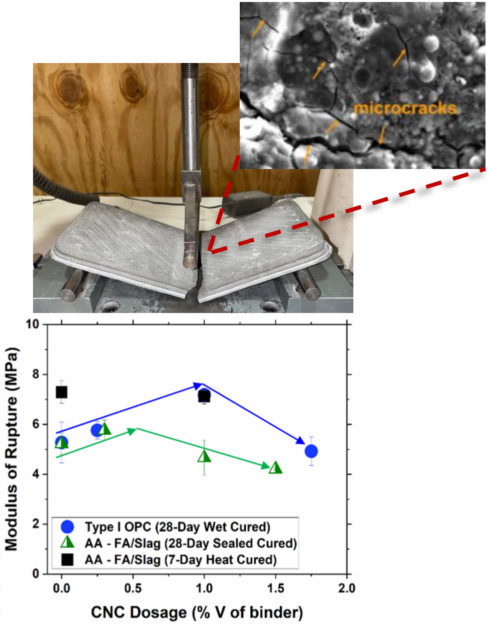
FPL



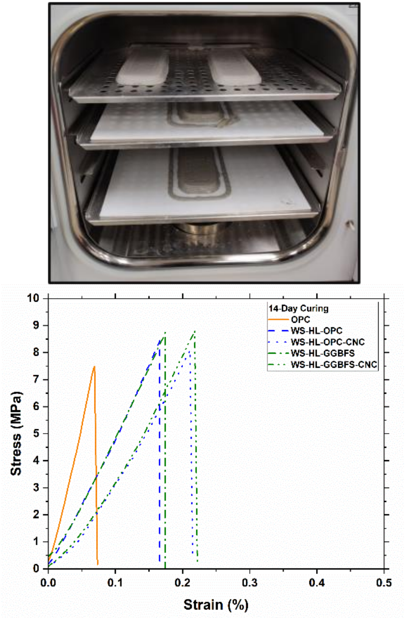
3D Printing of Sustainable Cementitious Composites



3D printed "alkali-activated- cellulose nanomaterial" composites



Structure-property relationship of 3D printed composites

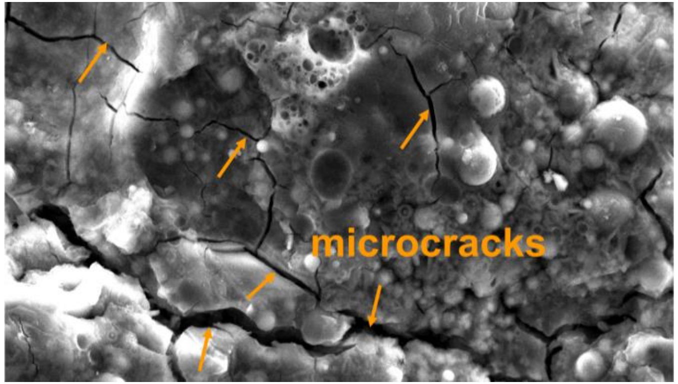


3D printed carbonatable cementitious materials

Research Approach

SCAN ME

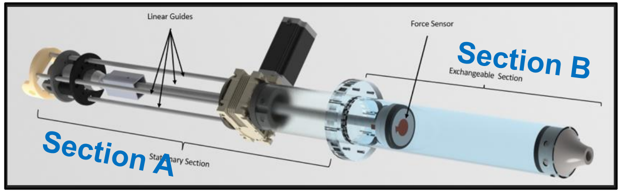
- Developing Printable Mixtures With CN-materials
- Impact of CN-materials on fresh properties
- Impact of CN-materials on performance and microstructure

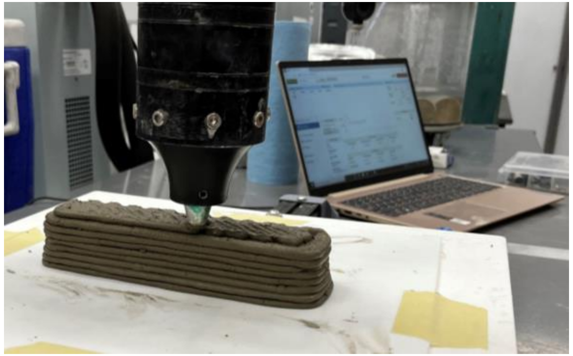


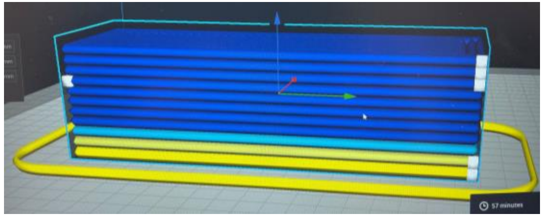
Printing Setup

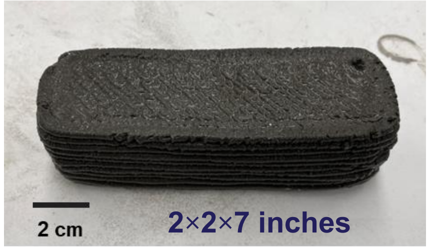
Temple University
College of Engineering

- The cartridge assembly was separated into two pieces (material can be easily loaded onto “Section B” and consolidated)
- The perimeter filament was printed in a straight-line pattern (5 mm/s) and the infill filaments were printed in a zigzag pattern (10 mm/s)



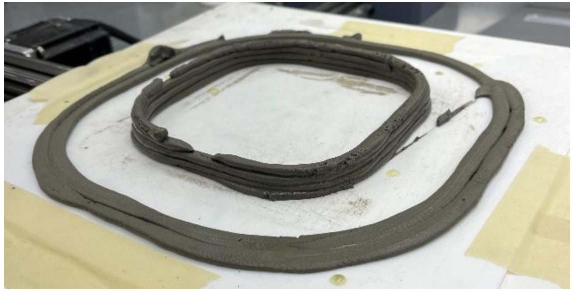


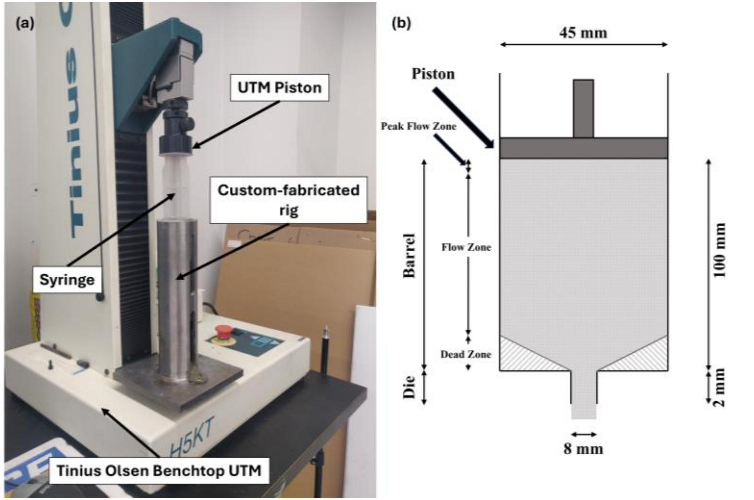


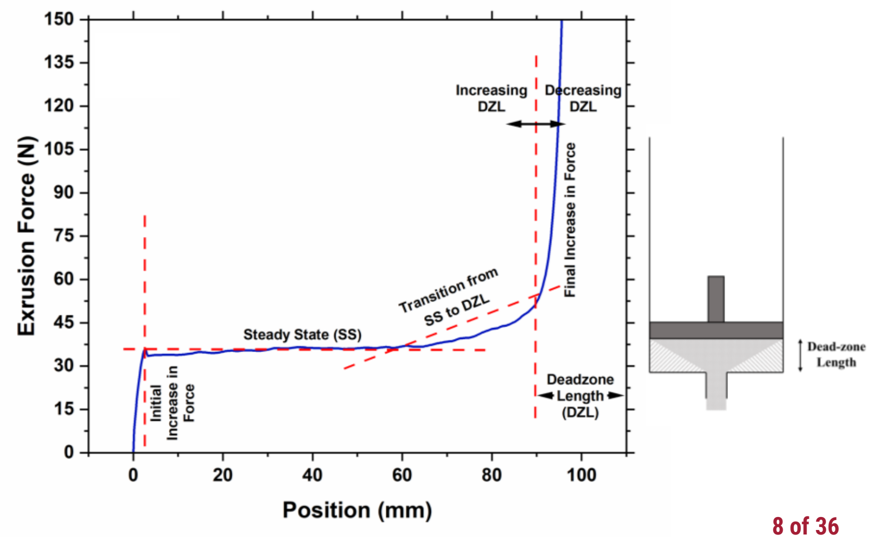


Printability Criteria

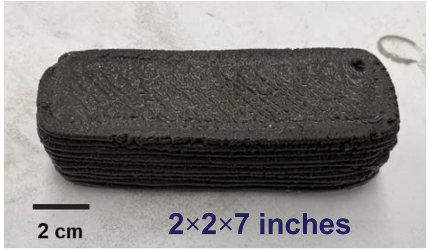
- The consistency of the extruded filaments (extrusion force)
- No splitting or tearing of the filament
- The number of successfully stacked layers before failure (e.g., 11 layers)
- Excessive water leak (i.e., open print time)







Printable Mixtures – AA versus OPC



- **Printable Mixtures with/without CNC**
  - AA precursor consists of 70% Class F FA and 30% GGBFS by mass
  - The CNCs were in aqueous suspension (10.6% solids)

OPC Systems

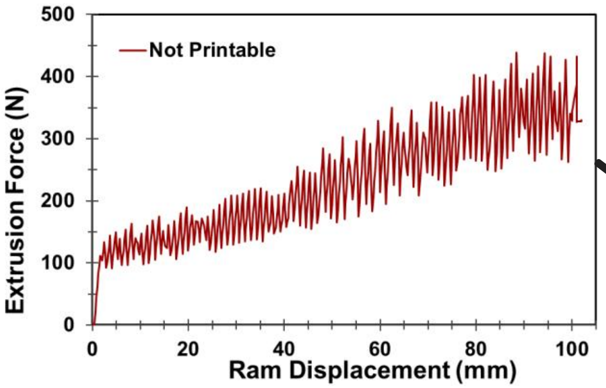
Mixture ID	Cement (g)	w/c	Water (g)	CNCs slurry (g)	VMA (g)	HRWR (g)	CNCs/cement (vol%)
OPC–Control	1200	0.26	312.00	0	21.60	9.84	0.00
OPC–0.25% CNC	1200	0.26	299.95	13.48	21.60	9.84	0.25
OPC–1.00% CNC	1200	0.26	263.81	53.91	14.40	12.00	1.00
OPC–1.75% CNC	1200	0.315	293.66	94.34	38.40	11.40	1.75

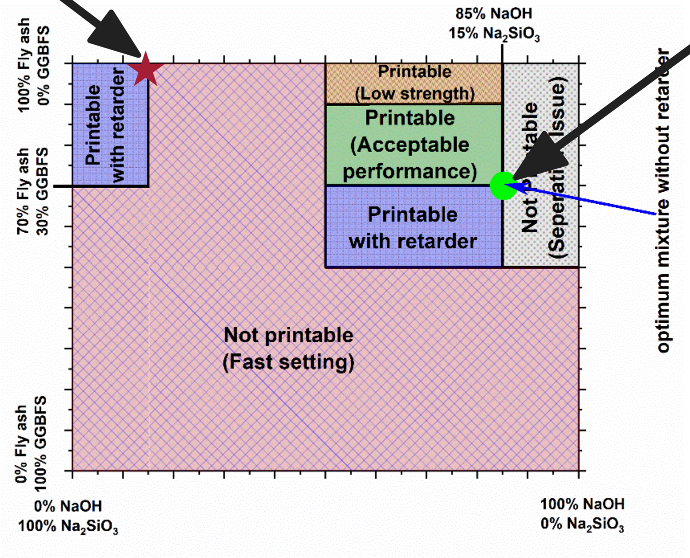
AA Systems

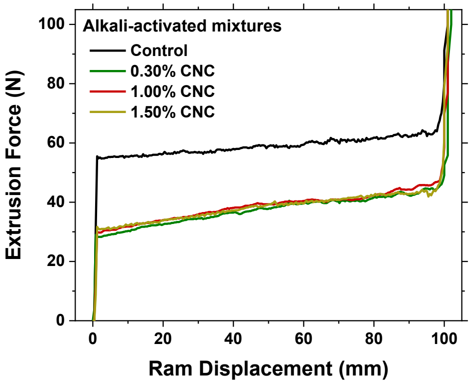
Mixture ID	FA (g)	GGBFS (g)	Liquid /binder	NaOH (g)	Na_2SiO_3 (g)	CNCs slurry (g)	CMC (g)	CNCs/binder (vol%)
AA–Control	840	360	0.32	326.40	57.60	0.00	6.00	0.00
AA–0.30% CNC	840	360	0.32	311.22	54.92	19.98	0	0.30
AA–1.00% CNC	840	360	0.335	291.10	51.37	66.59	0	1.00
AA–1.50% CNC	840	360	0.345	275.99	48.70	99.89	0	1.50

Extrudability and Buildability of Mixtures

Temple University
College of Engineering



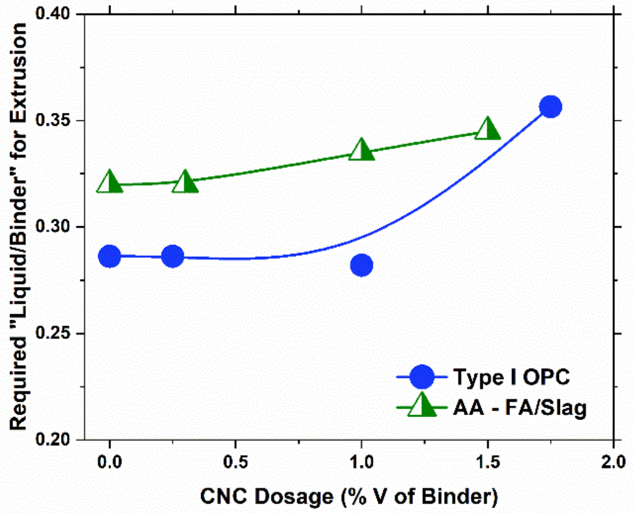




Extrudability and Buildability of Mixtures

Temple University
College of Engineering

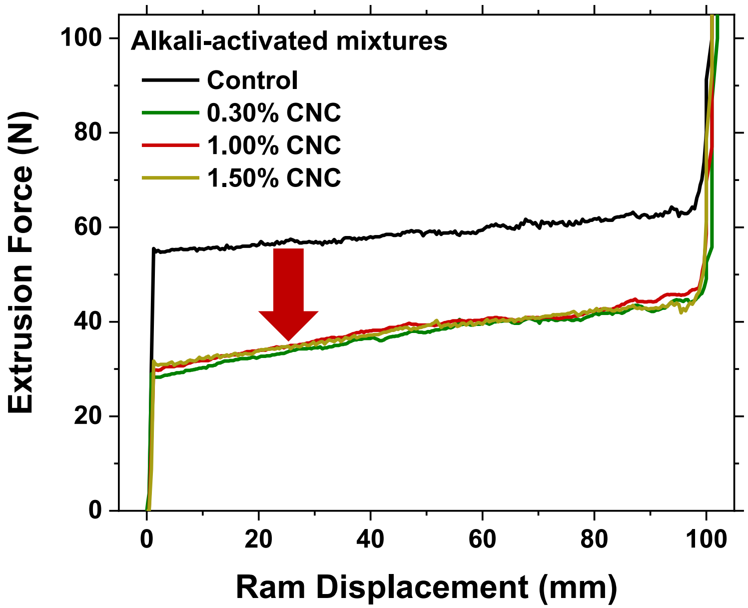
- The required “liquid/binder” was higher in AA mixtures compared to OPC mixtures
- However, OPC mixtures required a more dramatic increase of “liquid/binder” above 1.00% CNC concentration
- This can be attributed to the dispersion quality of CNC in different systems.

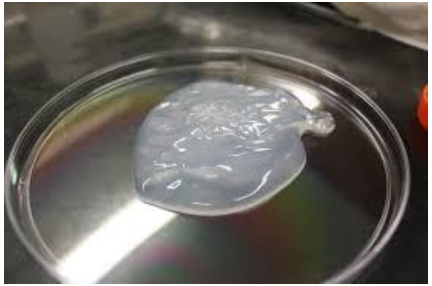


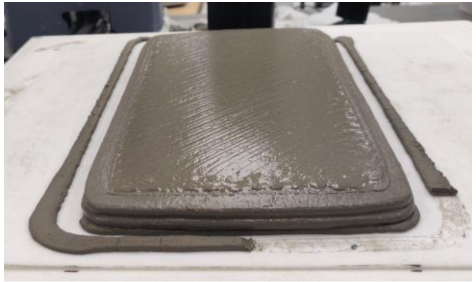
Extrudability and Buildability of Mixtures

Temple University College of Engineering

- The addition of CNC in AA mixtures reduces the extrusion pressure (i.e., CNC performs as a VMA in AA mixtures).



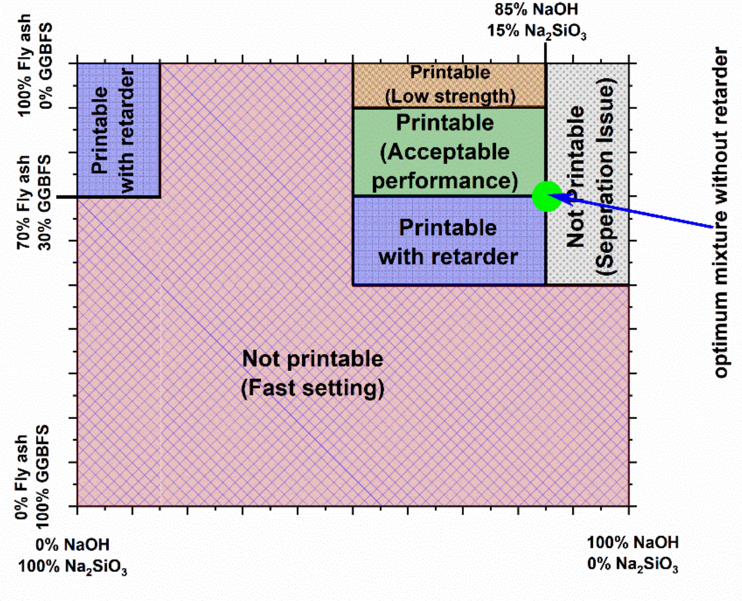




Extrudability and Buildability of Mixtures

Temple University College of Engineering

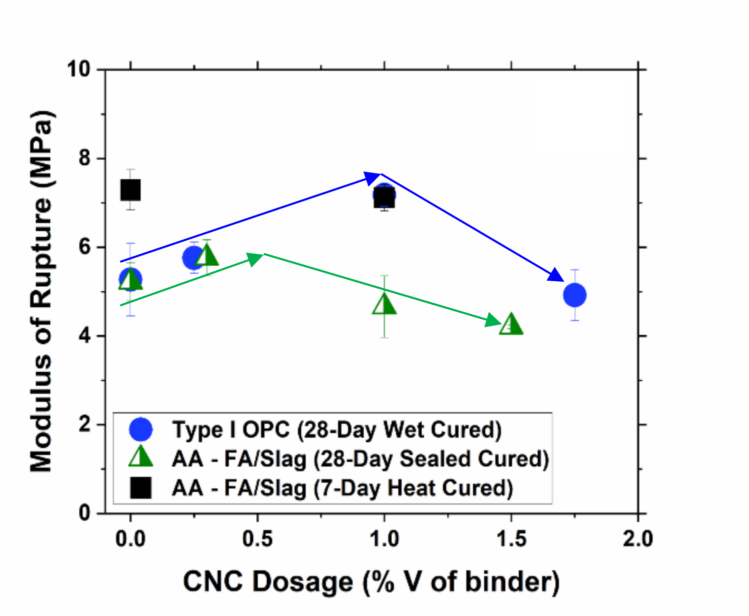
- The AA mixture without the addition of either CMC or CNC was not buildable. It seems that the CNC performs as a VMA in AA mixtures.
- The AA mixture with a "NaOH/Na_2SiO_3" mass ratio of 85:15 and a "FA/GGBFS" mass ratio of 70:30 was selected as the optimum AA mixture for printing.

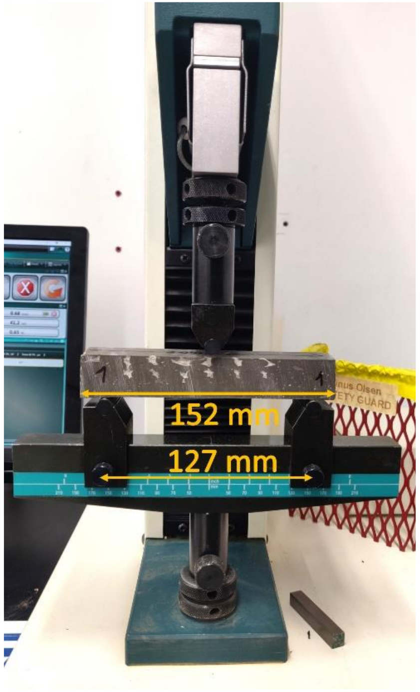


Mechanical Performance

Temple University
College of Engineering

- The inclusion of CNCs up to 1.00% (by volume of the binder) improves the overall mechanical performance

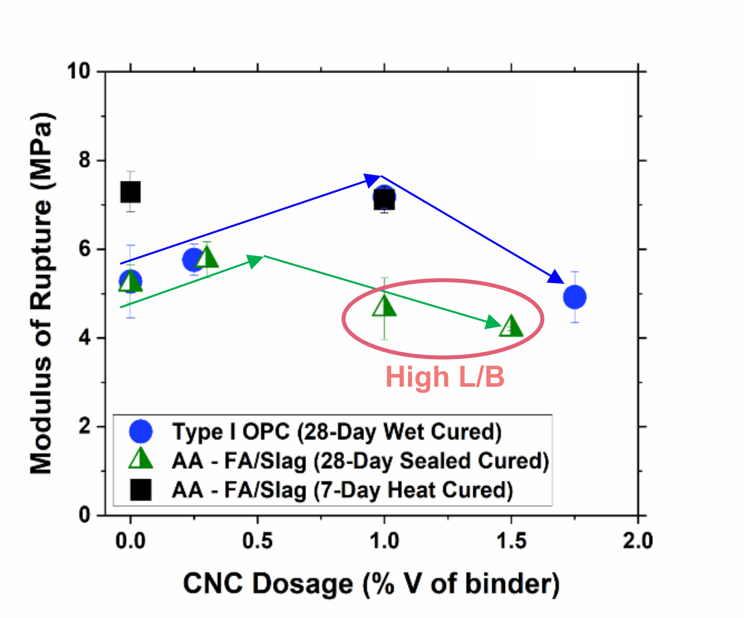


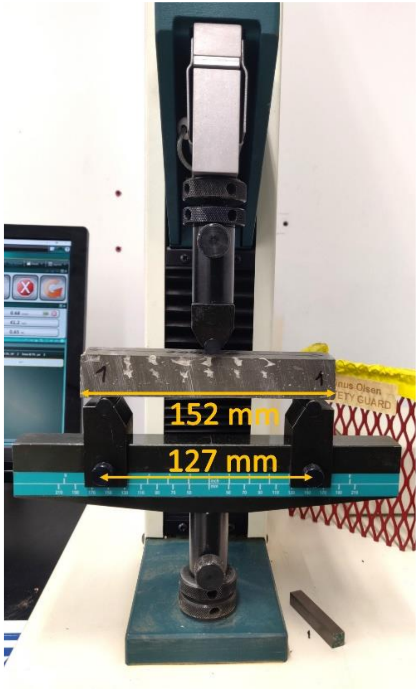


Mechanical Performance

Temple University
College of Engineering

- The inclusion of CNCs up to 1.00% (by volume of the binder) improves the overall mechanical performance

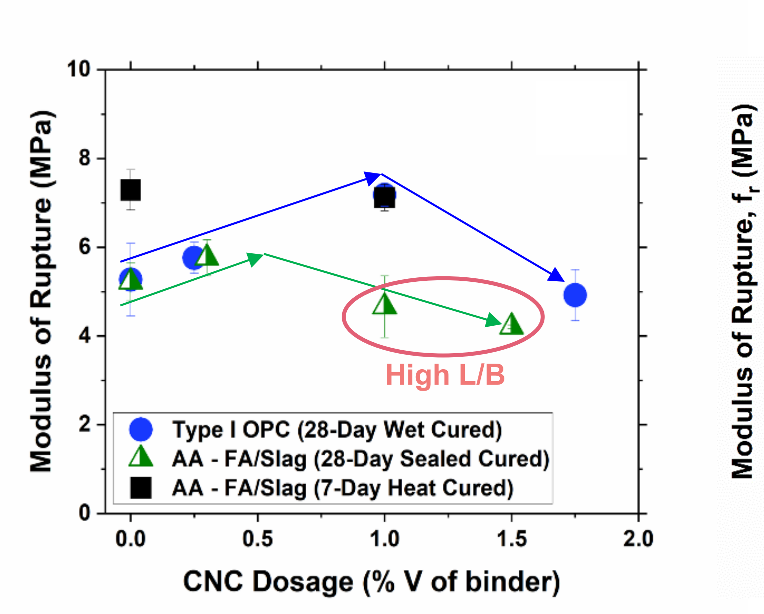


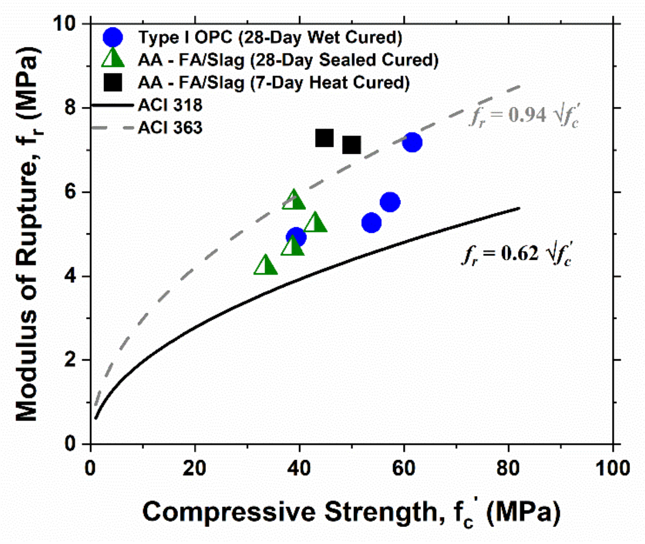


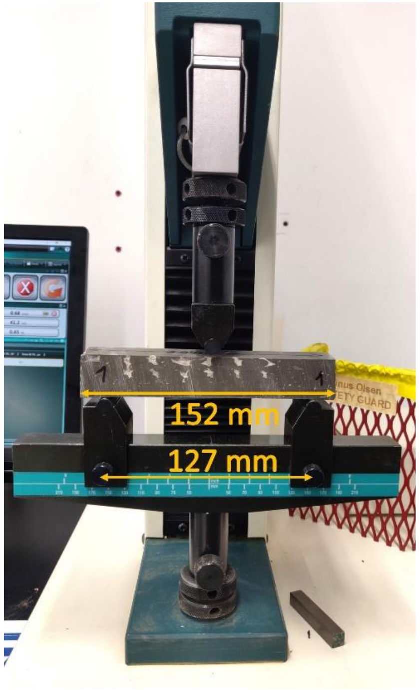
Mechanical Performance

Temple University College of Engineering

- The inclusion of CNCs up to 1.00% (by volume of the binder) improves the overall mechanical performance

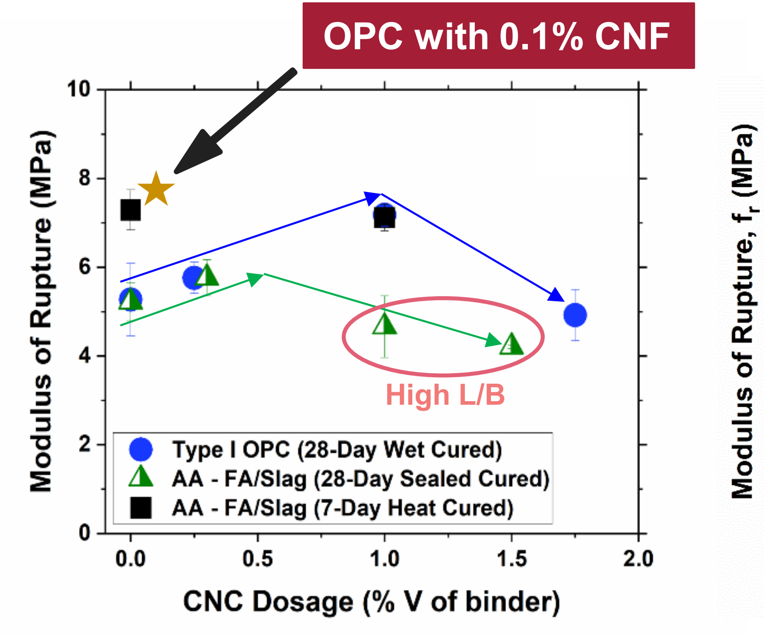


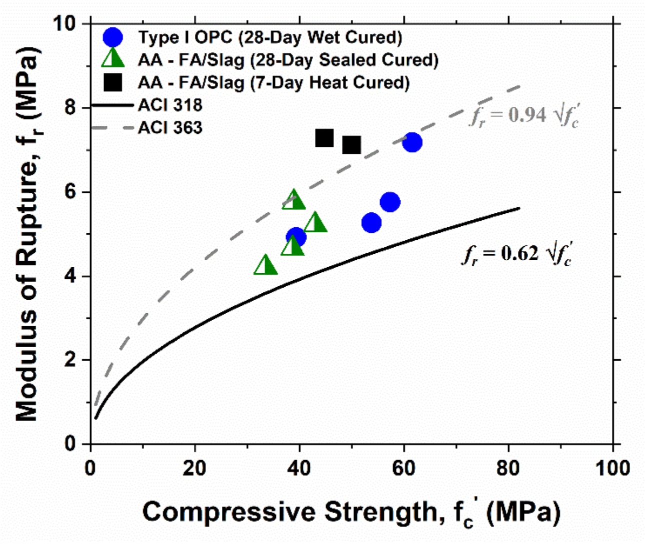


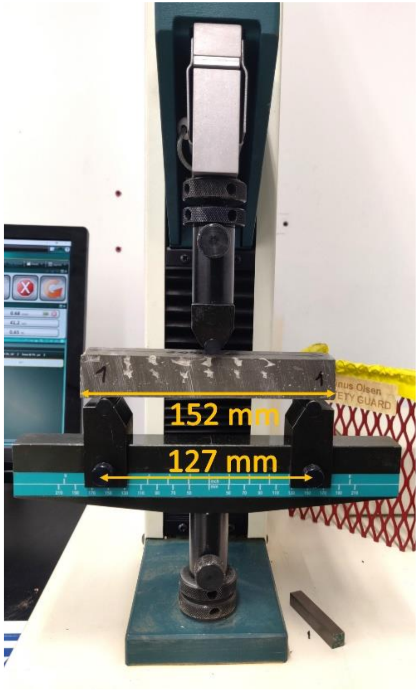


Mechanical Performance

- The inclusion of CNCs up to 1.00% (by volume of the binder) improves the overall mechanical performance



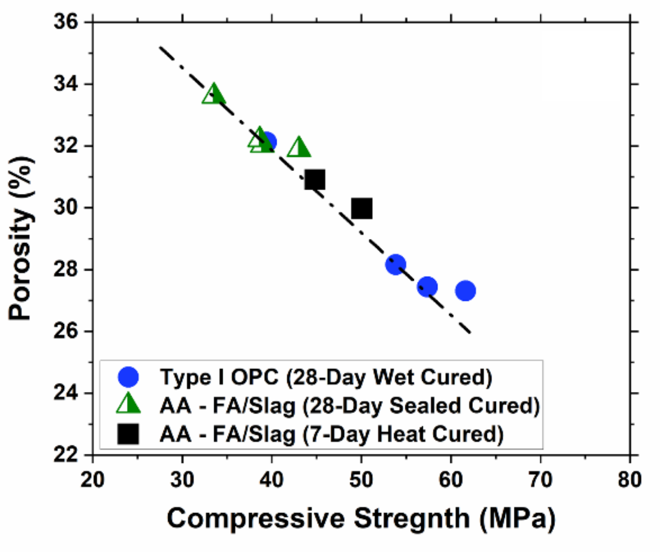




Porosity and Electrical Resistivity

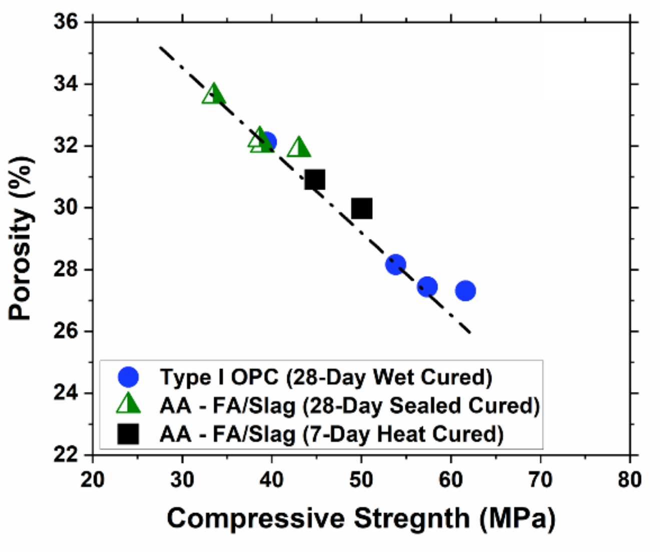
Temple University College of Engineering

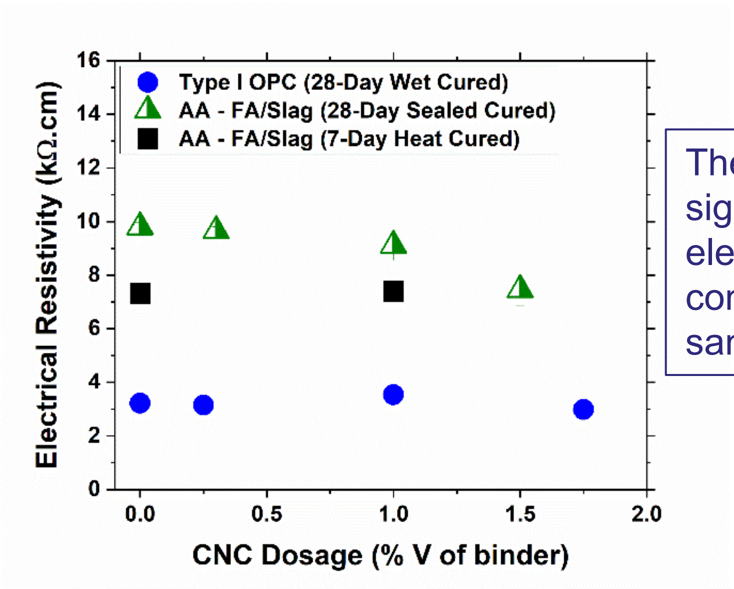
- There is a strong linear correlation between the porosity and compressive strength results



Porosity and Electrical Resistivity

- There is no significant change in the electrical resistivity of OPC samples with the addition of the different dosages of CNC.

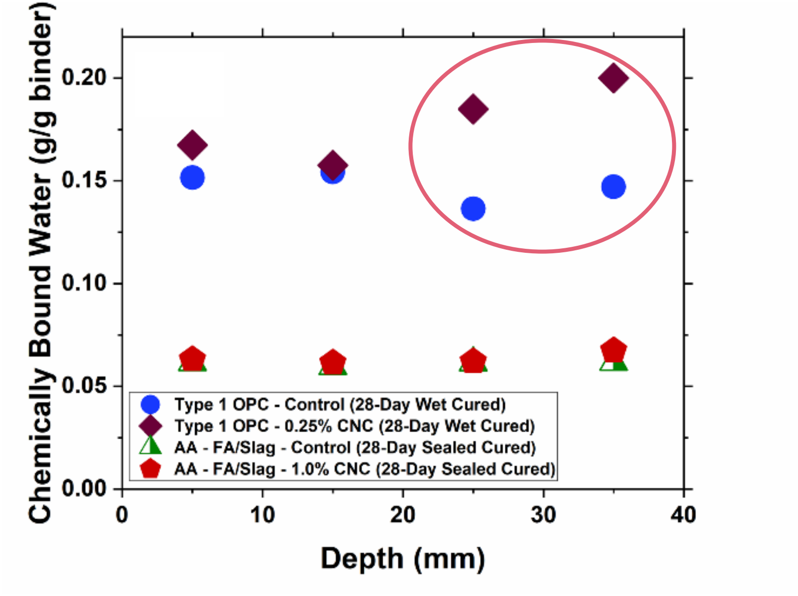




The AA samples have significantly higher electrical resistivity compared to OPC samples.

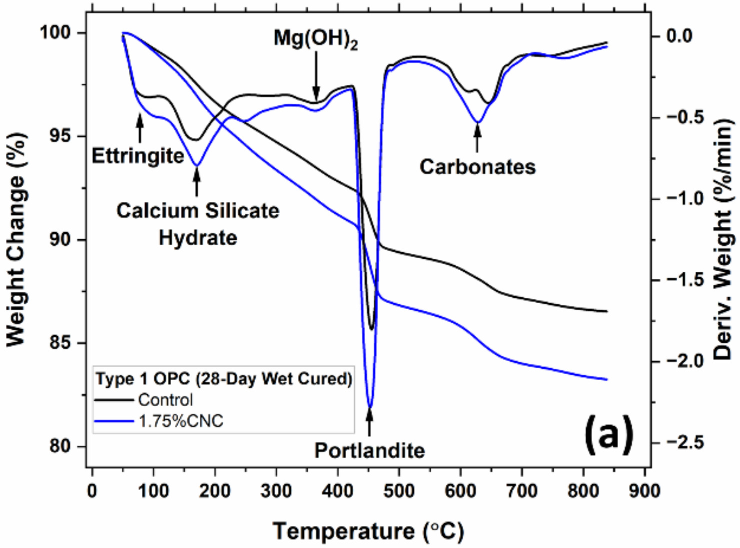
Chemically Bound Water

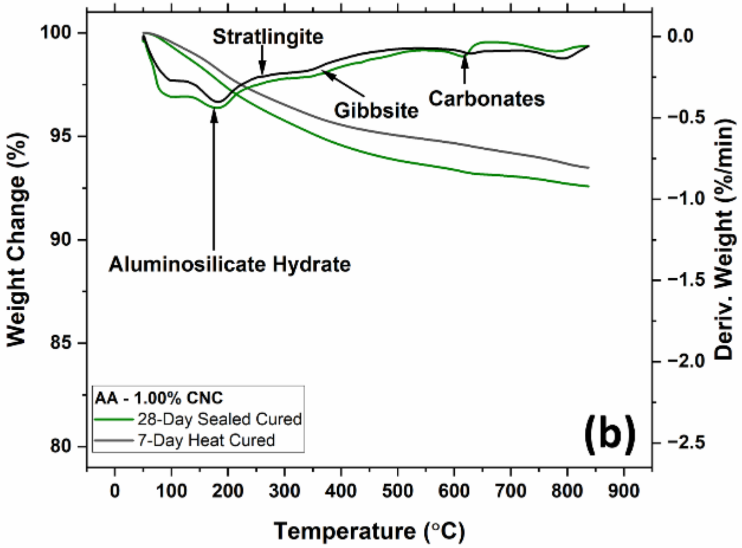
- OPC with 0.25% CNC approximately show a 25% increase in DOH.
- This is beneficial in low w/c systems such as 3D printed elements where the permeability of the matrix is low



Chemically Bound Water

- The OPC−CNC samples have higher chemically bound water content, suggesting that the addition of CNC improves the microstructure.

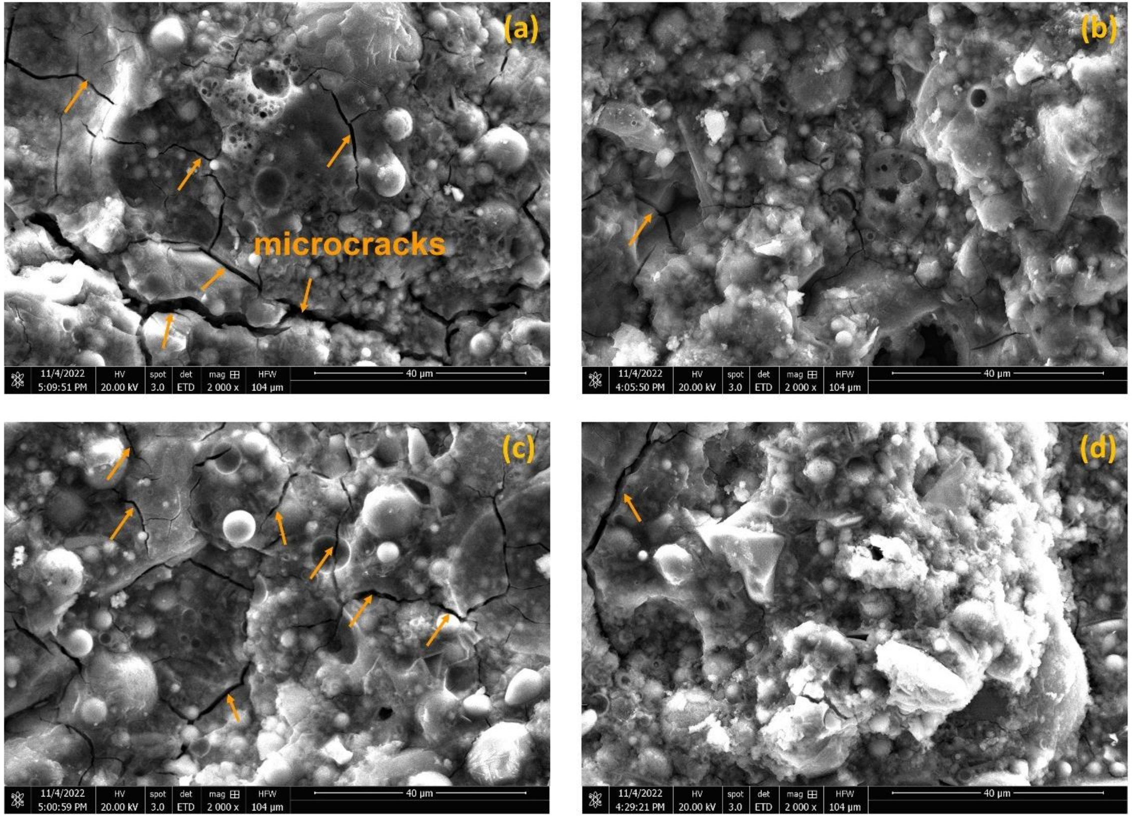




Microstructure Analysis

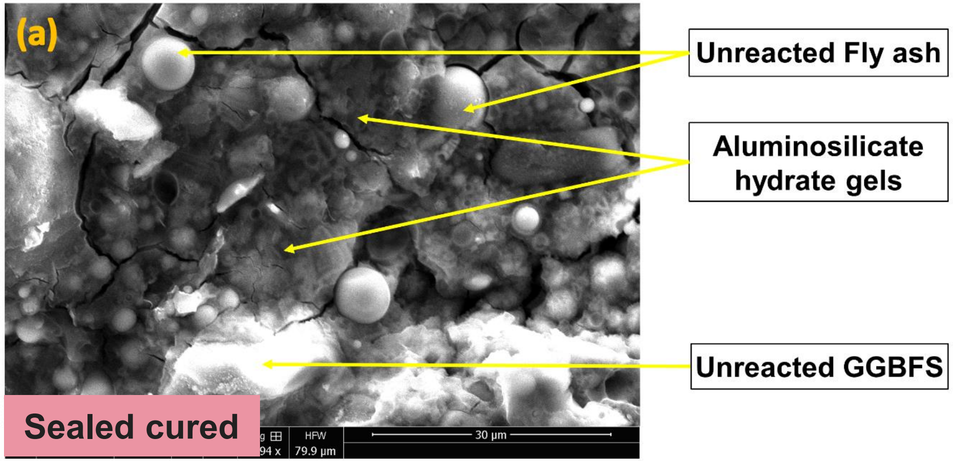
- The sealed-cured samples have a significantly higher amount of microcracks due to flexural stresses
- In heat-cured samples, the FA particles are well embedded and connected to the matrix.

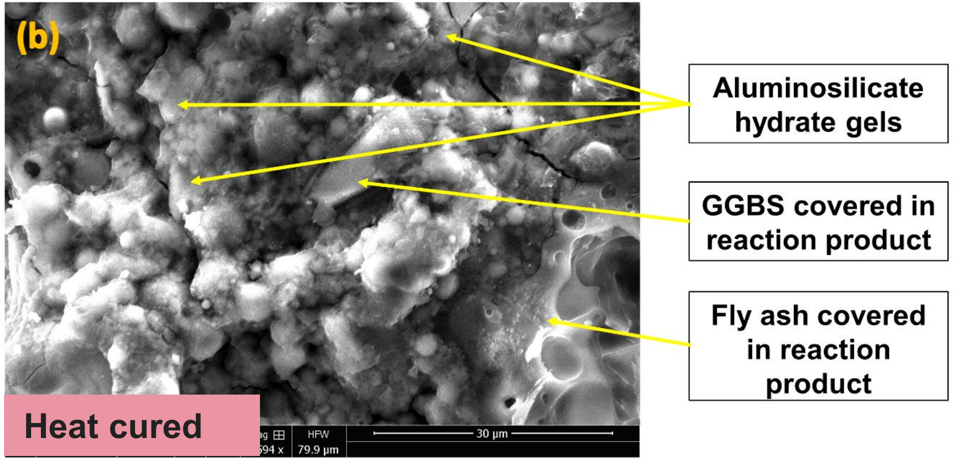
AA Sealed cured	AA Heat cured



Microstructure Analysis

- 28-day sealed cured samples show a higher amount of unreacted fly ash spheres
- Non-crosslinked N-A-S-H and C-A-S-H or crosslinked C-N-A-S-H are the main reaction product





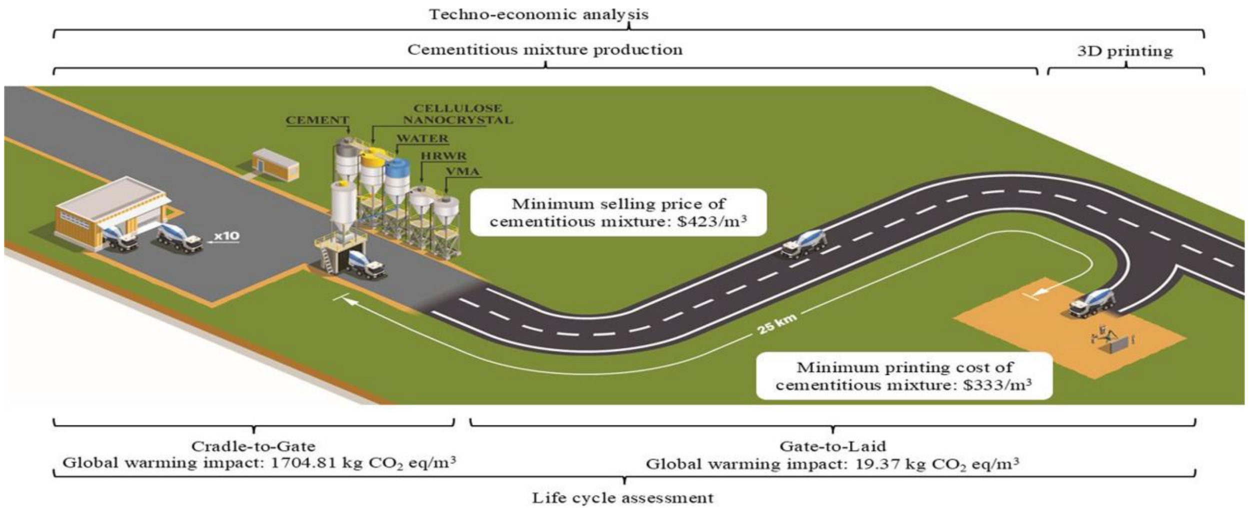
Techno-Economic Analysis

SCAN ME

- The potential to eliminate or reduce the need for chemical admixtures (e.g., viscosity modifiers)
- Impact of CN-materials on the performance of 3D printed elements
- Replacing the ordinary portland cement with waste materials (fly ash and slag)
- Reductions in both the capital and operating costs potentially result from the application of the 3D printing process.

Cost and Environmental Impact

- The estimated minimum selling price (MSP) and environmental impact of the CNC-reinforced cementitious mixtures were lower than those of the conventional cementitious mixture when compressive and flexural strength were considered as functional units.



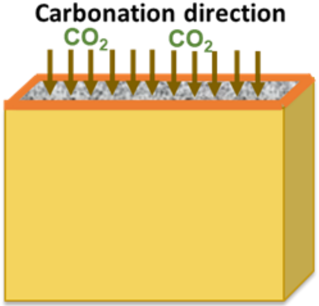
3D Printable Carbonatable Cementitious Materials

SCAN ME

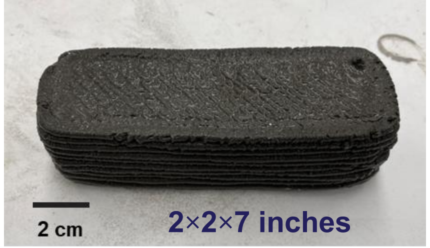
Motivation

- The development of novel building materials that store more carbon than emitted during manufacture (toward carbon-negative structural components).
- The production of concrete materials through binder carbonation (i.e., CO_2 mineralization) has the potential to consume approximately two billion tons of CO_2 annually.

$$CaSiO_3 + CO_2 + H_2O \rightarrow CaCO_3 + SiO_2 + H_2O$$



Printable Mixtures w/wo CNC



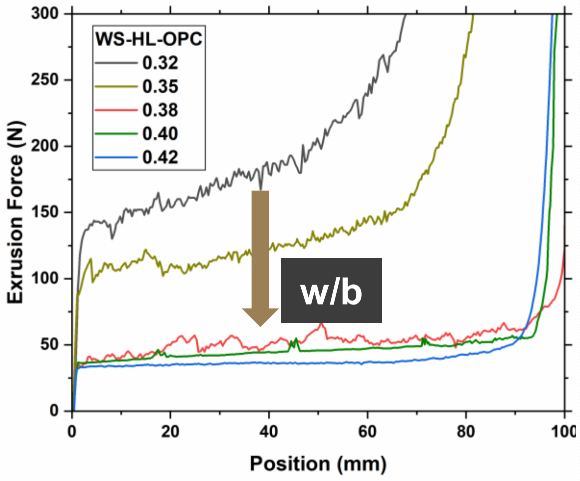
- Four different CCM paste mixtures with varying CNC concentrations with a w/b of 0.42 were prepared
- 55% of wollastonite replaced with 15% hydrated lime, and the remaining 30% with either OPC or GGBFS, to achieve buildable and extrudable mixtures
- The CNCs were in aqueous suspension (10.6% solids)

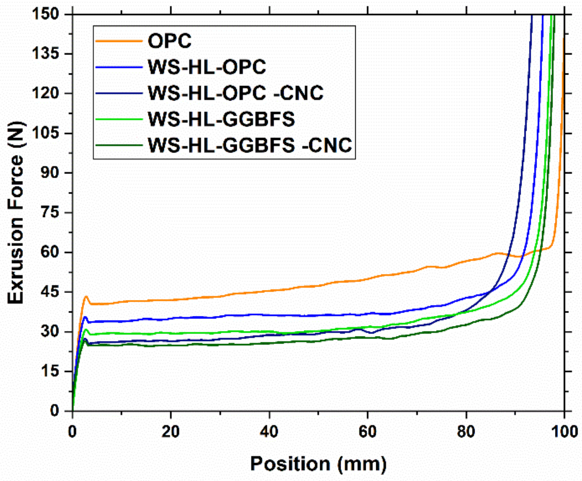
Mixture ID	Method of curing	OPC (g)	WS (g)	GGBFS (g)	HL (g)	w/b	Water (g)	VMA (g)	HRWR (g)	CNCs/cement (vol%)
OPC	Wet-cured	500	0	0	0	0.26	130.00	9.00	4.10	0.00
WS-HL-OPC	CO_2-cured	150	275	0	75	0.42	210.00	10.00	0.00	0.00
WS-HL-GGBFS	CO_2-cured	0	275	150	75	0.42	210.00	10.00	0.00	0.00
WS-HL-OPC-CNC	CO_2-cured	150	275	0	75	0.42	204.68	10.00	0.00	0.25
WS-HL-GGBFS-CNC	CO_2-cured	0	275	150	75	0.42	204.68	10.00	0.00	0.25

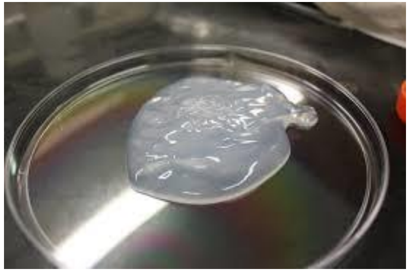
Extrudability and Buildability of Mixtures

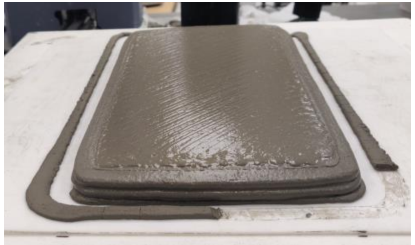
Temple University College of Engineering

- The addition of CNC in CCM mixtures reduces the extrusion pressure (i.e., CNC performs as a VMA in these mixtures).



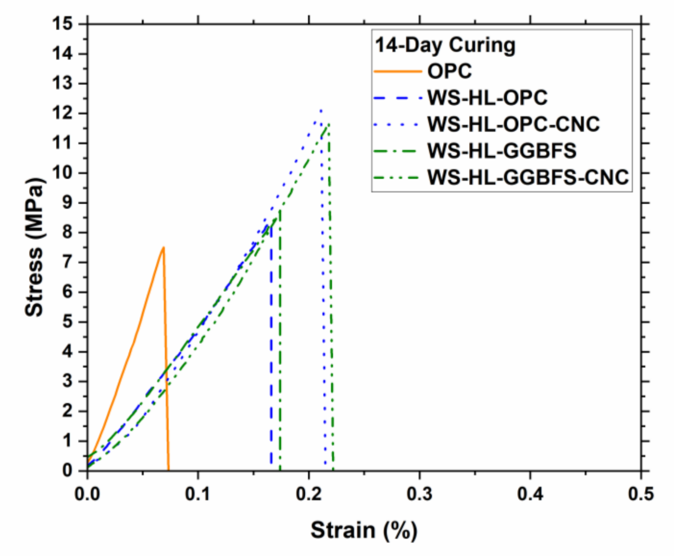


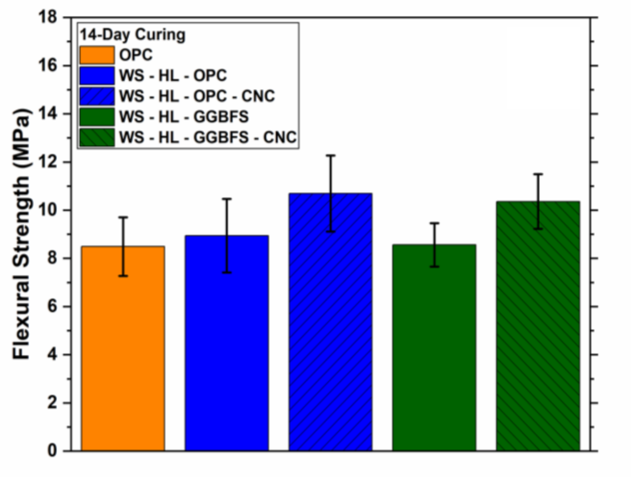


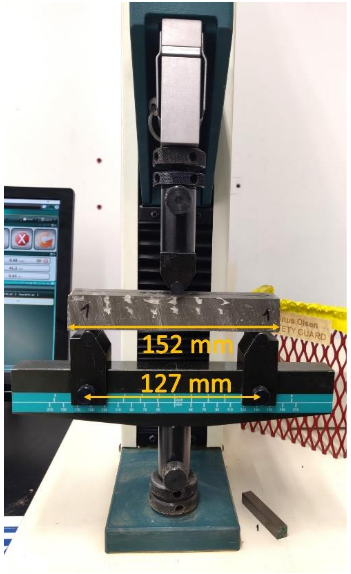


Mechanical Performance

- The flexural strength of CCM systems is comparable to that of OPC samples at 14 days
- CNC-based CCM samples exhibit approximately 25% higher flexural strength

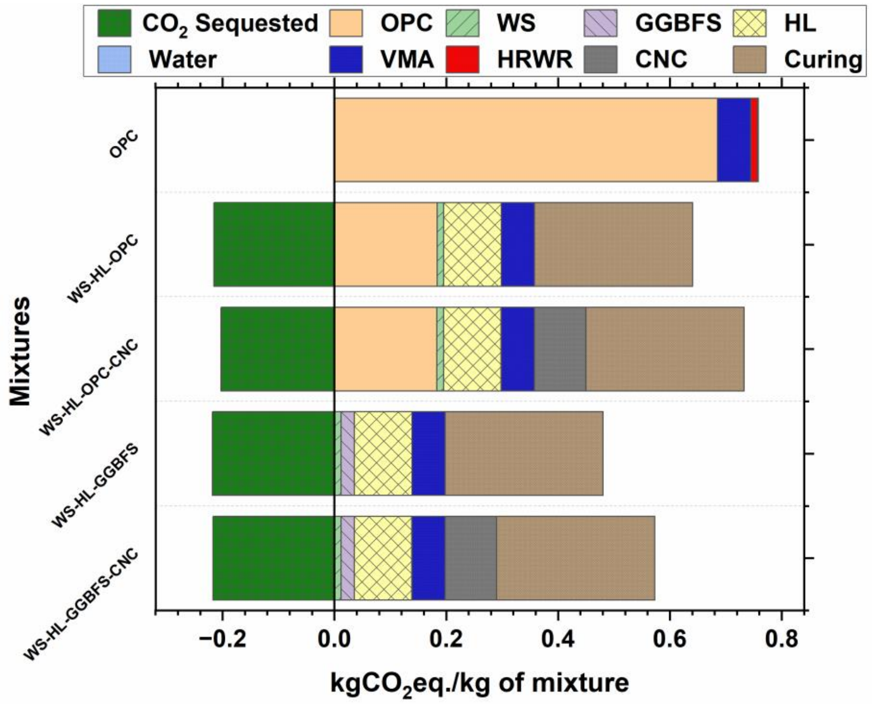






Environmental Impact

- CCM mixtures demonstrate a substantial reduction in net emissions owing to the sequestration of CO_2 during curing
- WS-HL-GGBFS results in the lowest total emissions (a 65% reduction compared to the control OPC mixture)



Conclusions

- The printability of the AA mixtures was improved by increasing the dosage of CNC, suggesting that the CNC performs as a viscosity-modifying agent in AA mixtures.
- The inclusion of CNCs up to 1.00% (by volume of the binder) improves the overall mechanical performance and reduces the porosity of 3D-printed OPC and heat-cured AAM samples.
- The developed printable “alkali-activated-CNC” composites can provide an overall reduction in the environmental impacts of the 3D-printed cementitious composites by eliminating/reducing the need for different chemical admixtures.

Conclusions

- After 14 days of carbonation, the CCM systems achieve a 60-70% degree of carbonation. X-ray diffraction patterns revealed the formation of calcite and aragonite as the primary phases in the CCM samples.
- The flexural strength of the 3D-printed CCMs becomes comparable to that of OPC after 14 days. The inclusion of CNC results in a further increase in flexural strength, likely attributed to the crack-bridging mechanism of CNC fibers.
- The developed 3D-printable ternary CCMs in combination with CNCs can significantly reduce the environmental impacts of 3D-printed cementitious composites.

Acknowledgements

NSF

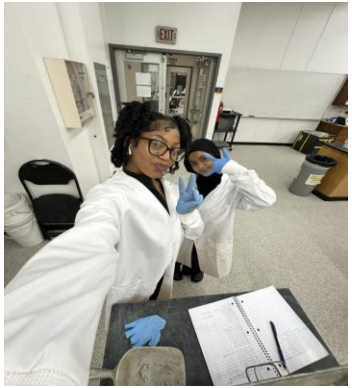
pennsylvania
DEPARTMENT OF COMMUNITY & ECONOMIC DEVELOPMENT

U.S. Endowment for Forestry and Communities

Forest Products Laboratory

TAKTL

Acknowledgements



Thank You!

Mehdi Khanzadeh, PhD, PE

Mehdi.Khanzadeh@temple.edu