VANDERBILT
School of Engineering

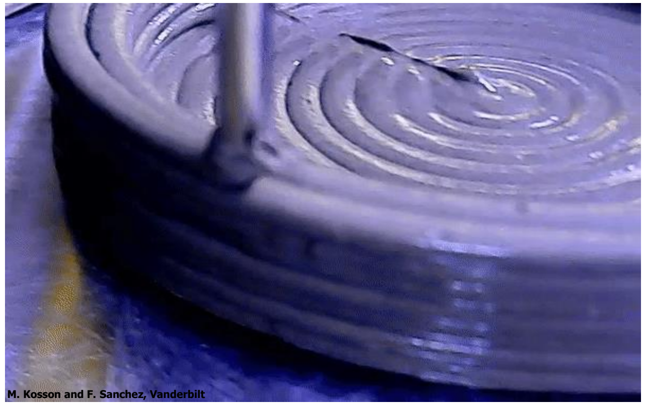
Civil and Environmental Engineering

Effect of Halloysite Nanoclay on the Performance of 3D Printed Cement-Based Materials

M. Kosson,[1] L. Brown,[2] and F. Sanchez,[1,2]

Civil and Environmental Engineering Department

Chemical and Biomolecular Engineering Department

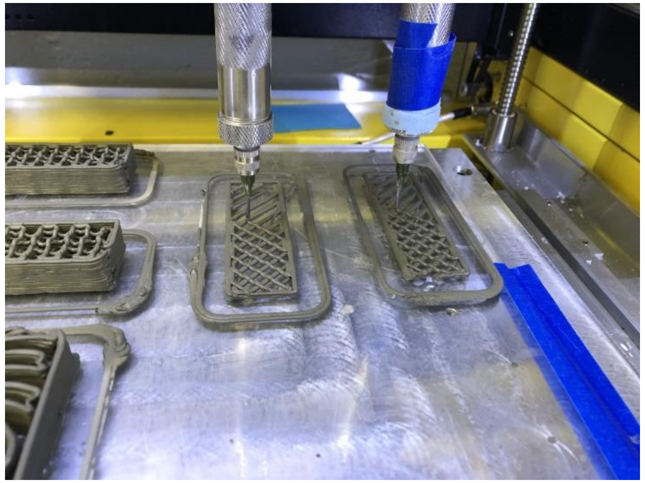


ACI Spring 2024 Convention, March 26, 2024
Session: Application of Nanoparticles in 3D Printed Concrete

3D Printing with Cement

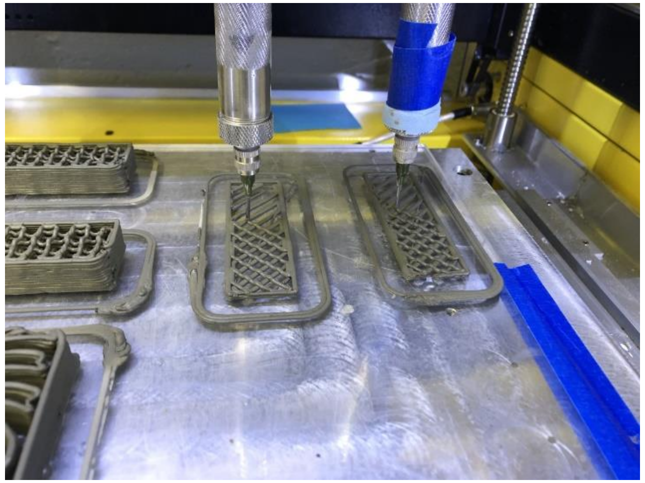
- Construction scale printing
  - Fabrication of large-scale elements and structures
  - Improving construction process: increase in productivity, construction speed, design flexibility, architectural freedom, and reduction of waste
  - Adaptation of traditional cement-based mixtures
  - Large filament layers and limited geometric control
- Creating/designing novel materials
  - Exploration of innovative cementitious formulations
  - Optimizing microstructure for targeted performance (e.g., functionally graded materials)
  - Implementing hierarchy of structures and patterns

Image: Shutterstock



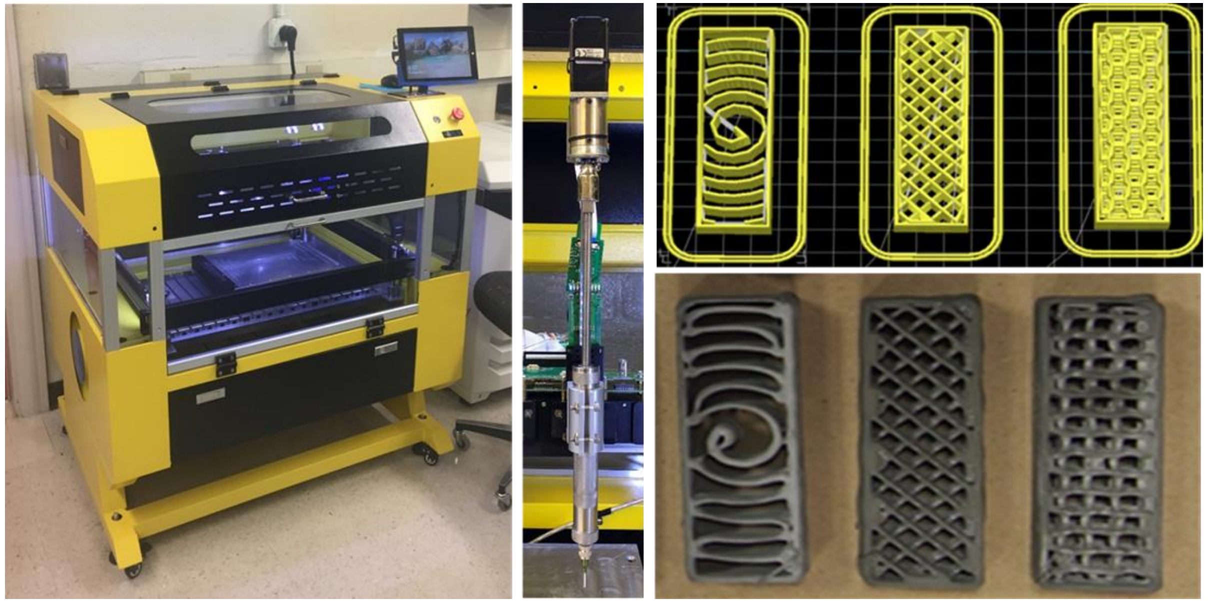
3D Printing with Cement

- Construction scale printing
  - Fabrication of large-scale elements and structures
  - Improving construction process: increase in productivity, construction speed, design flexibility, architectural freedom, and reduction of waste
  - Adaptation of traditional cement-based mixtures
  - Large filament layers and limited geometric control
- Creating/designing novel materials
  - Exploration of innovative cementitious formulations
  - Optimizing microstructure for targeted performance (e.g., functionally graded materials)
  - Implementing hierarchy of structures and patterns



---> 3D Printed Architected Concrete

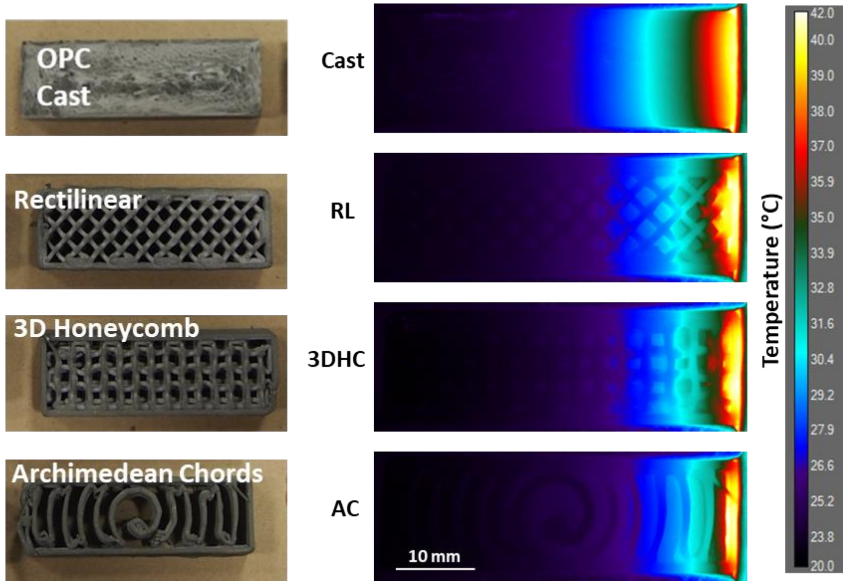
3D Printing of Architected Concrete



- Hydra 430 (Hyrel 3D)
  - Gantry-style 3D printer
  - 400 mm x 300 mm x 250 mm build area
  - 60 µm positional accuracy
- EMO-XT Printing Head
  - Designed for paste extrusion
  - 25 mL paste reservoir
  - 1.6 mm nozzle tip

3D Printed Architected Concrete

- Tailoring geometry and composition to manipulate properties
  - Customization of mechanical properties - e.g., stiffness and impact absorption
  - Control of crack propagation for enhanced structural integrity
  - Optimization for thermal storage and efficient thermal transfer for energy management
- Expand the design space
  - Need to understand link between geometry, composition, and material properties
  - Need to understand filament formation and properties



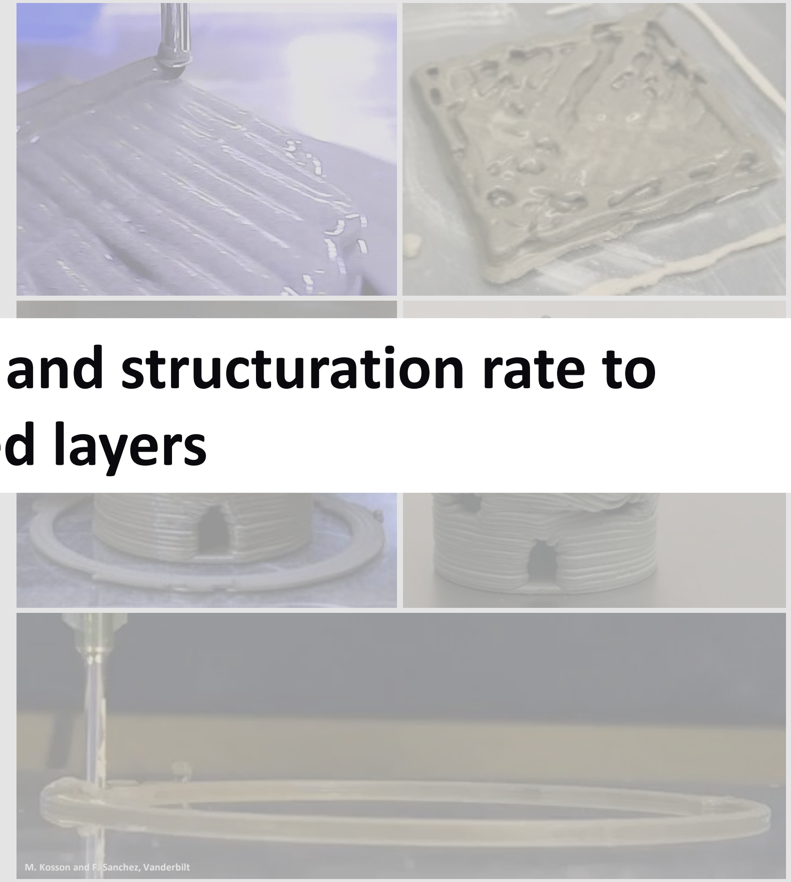
Kosson et al., submitted

Printability Requirements

- Extrudability – Sufficiently fluid and pumpable for extrusion
- Workability and flowability – Pass through the printing nozzle without discontinuity to be placed in layers

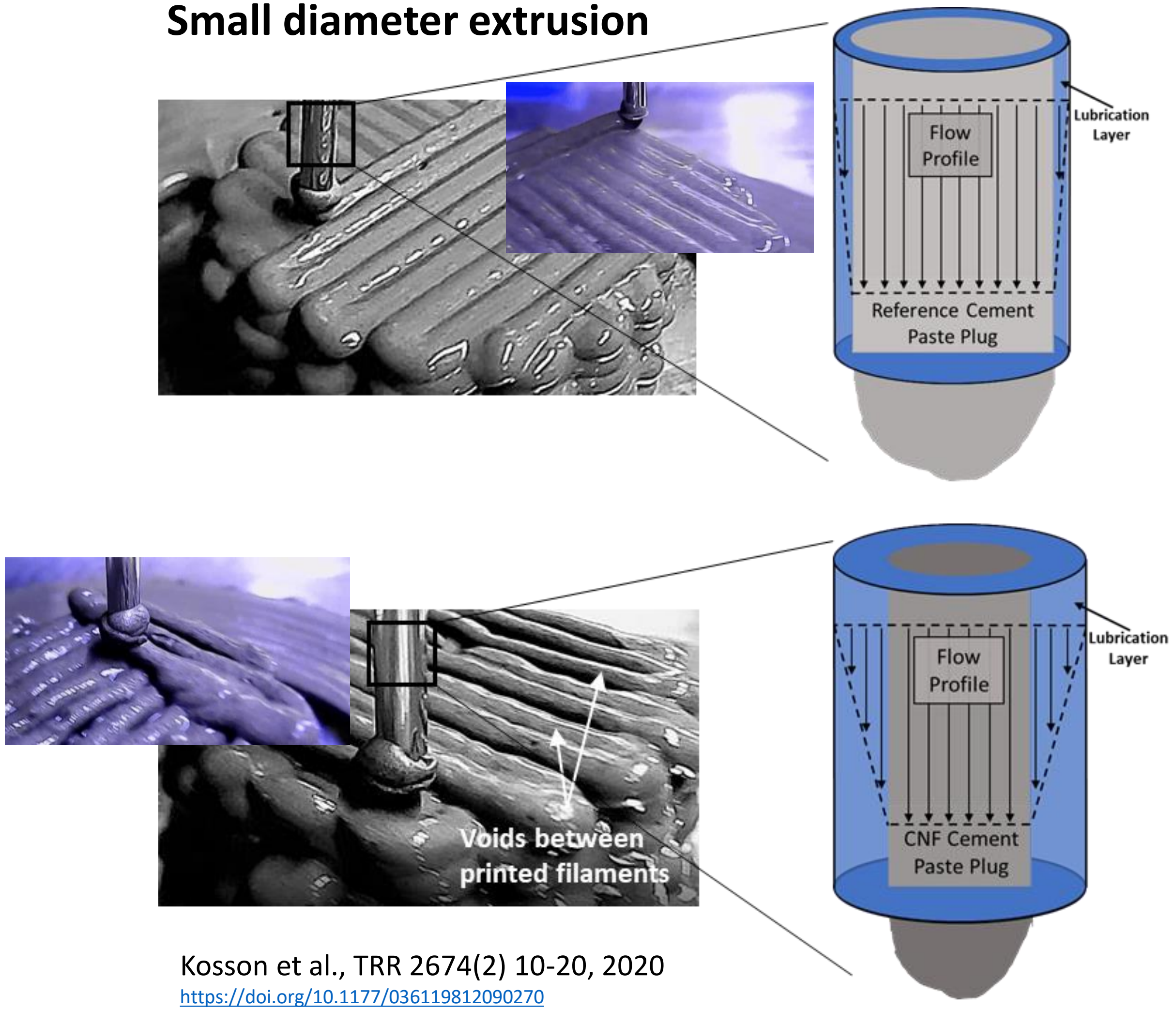
Greater control of the hydration kinetics, rheology, and structuration rate to ensure buildability and shape stability of the printed layers

- Open time for placement – Change of flowability with time
- Set rapidly and have high resistance to adhesive failure



Small Diameter Extrusion Impact

Small diameter extrusion



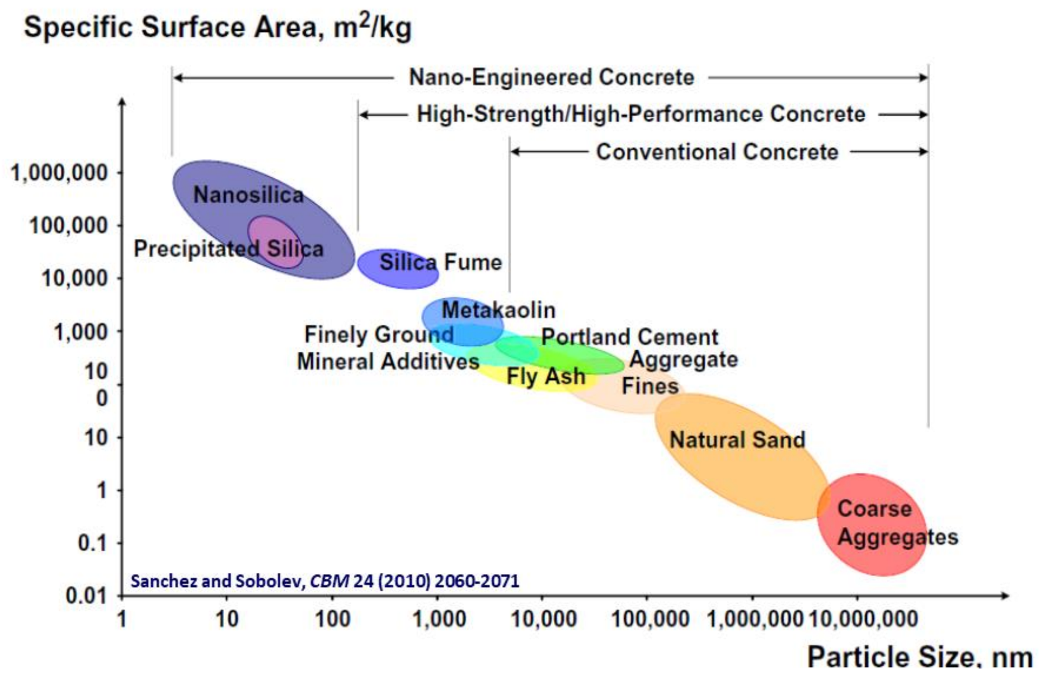
Kosson et al., TRR 2674(2) 10-20, 2020
https://doi.org/10.1177/036119812090270

- Admixture and inclusion types affect the formation of the extruded filament
- Dynamic evolution of the cement ink during extrusion
  - Liquid phase filtration due to pressure inside the 3D print head
  - Formation of a lubrication layer

---> Dynamic evolution of w/c ratio

Nanoparticle Benefits in Concrete

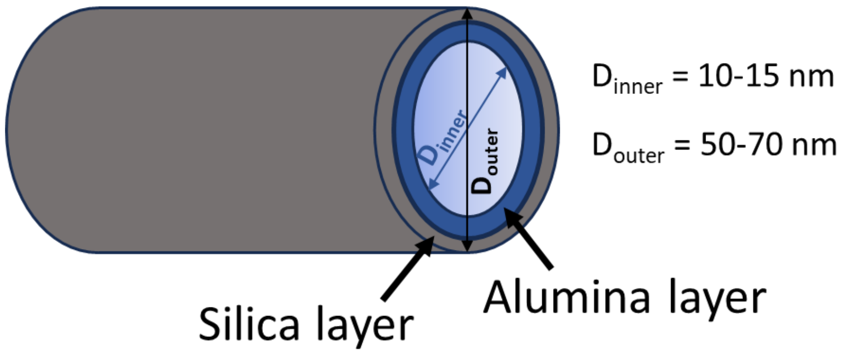
- Improved control of rheology and setting rate
- Microstructural densification (reduced porosity)
- Improved mechanical performance and durability
- Novel properties (e.g., self-sensing, self-cleaning)



---> Role and effectiveness of nanoparticles in the context of 3D printing?

Halloysite Nanoclay (HNC)

- Naturally occurring mineral with a two-layered tube structure – outer silica, inner alumina
- 50-70 nm diameter, 1-3 µm length, large surface area: 64 m^2/g
- Benefits: enhanced rheology and setting rates, increased thixotropy, improved paste cohesion, potential for nano-reinforcement



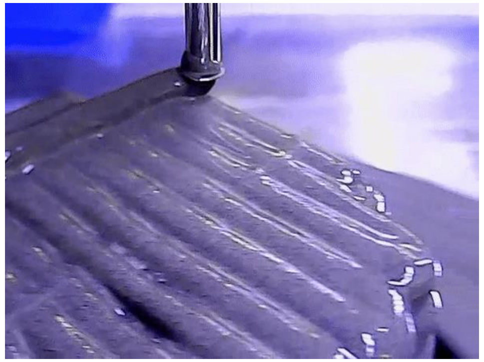
Objective: Investigate the impact of halloysite nanoclay (HNC) incorporation on the properties of hardened filaments and printed structures

3D Printed Materials

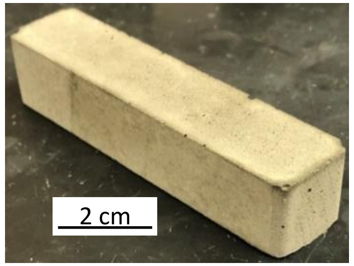
- Ink formulations
  - Type I/II Portland cement
  - With and without 5% cement replacement with HNC
  - 0.3 w/c ratio; 0.5 w/c ratio; high-range water reducer; viscosity modifier; anti-washout admixture
- Specimen types
  - Rectilinear columns (100% infill)
  - Concentric beams (100% infill)
  - Cast companion specimens

Cast Column

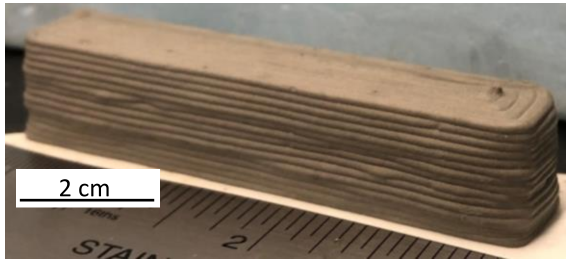
3D Printed Column



Cast Beam

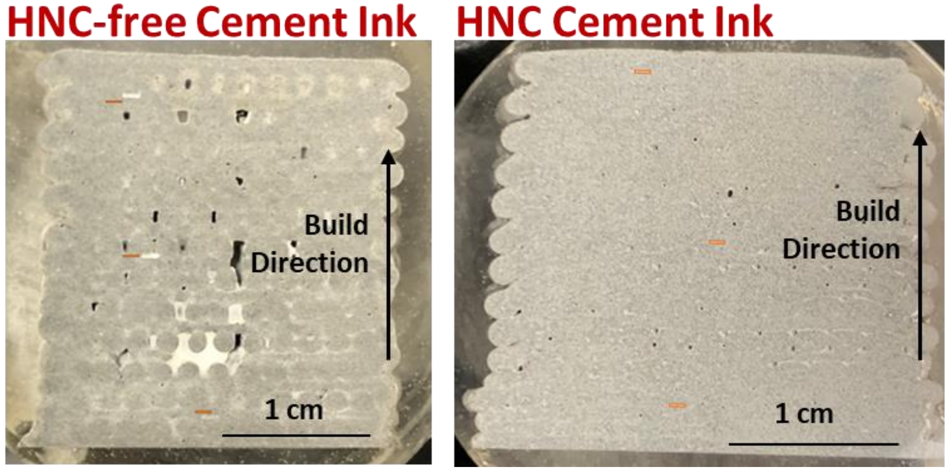


3D Printed Beam

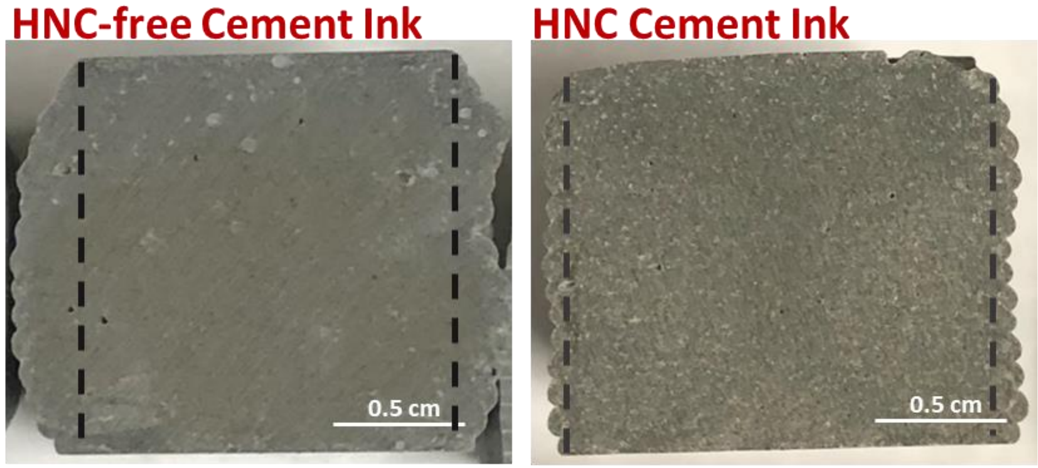


3D Printed Filament Formation and Morphology

Extrudability



Buildability

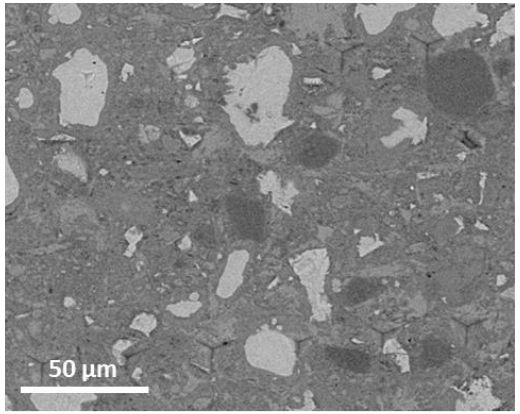


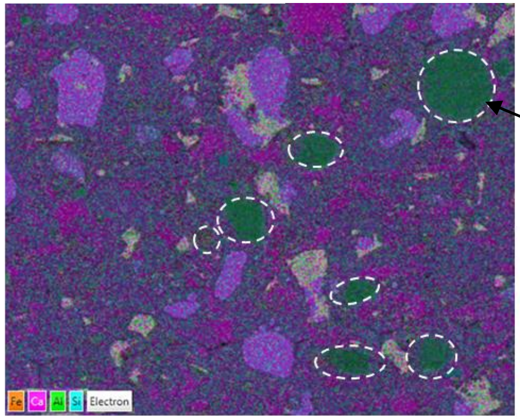
- Improved extrusion consistency with HNC, reducing printing discontinuities and underextrusion
- Decreased air voids and larger pores with HNC
- Enhanced ink viscosity and minimized water segregation with HNC
- Improved buildability and decreased deformation with HNC

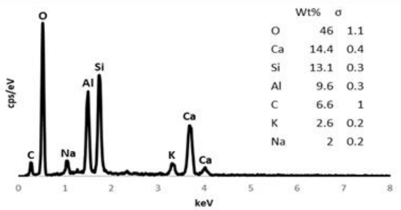
3D Printed Filament Microstructure

HNC Cement Ink

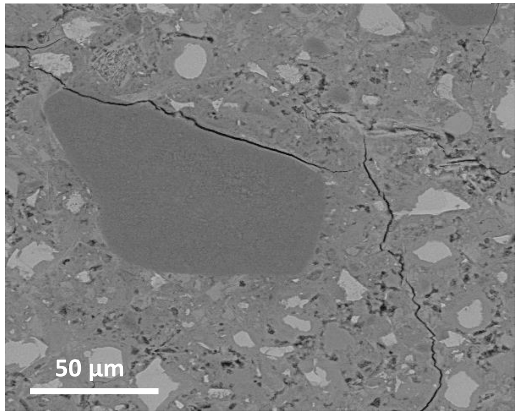
3D Printed Filaments







Cast (w/s = 0.3)

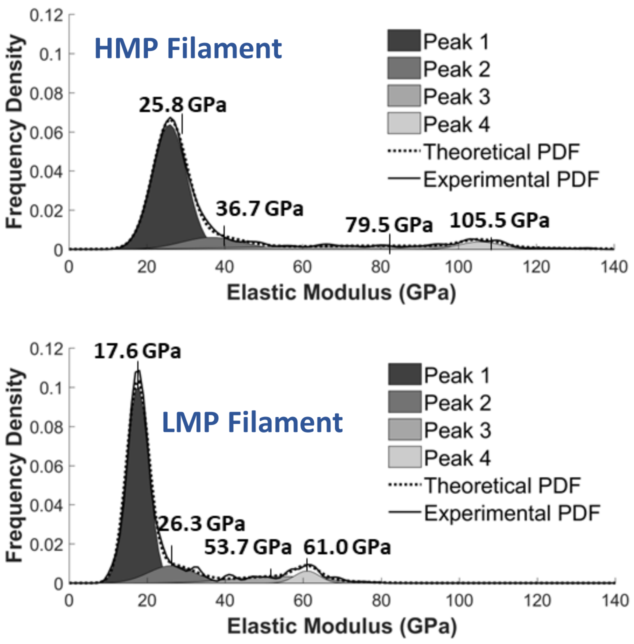


- Presence of HNC clusters intermixed with hydrates
- Image analysis revealed a 20% variation in HNC cluster numbers among printed filaments, indicating migration during extrusion
- Cast specimens had larger clusters, suggesting 3D printing helped breaking up HNC clusters

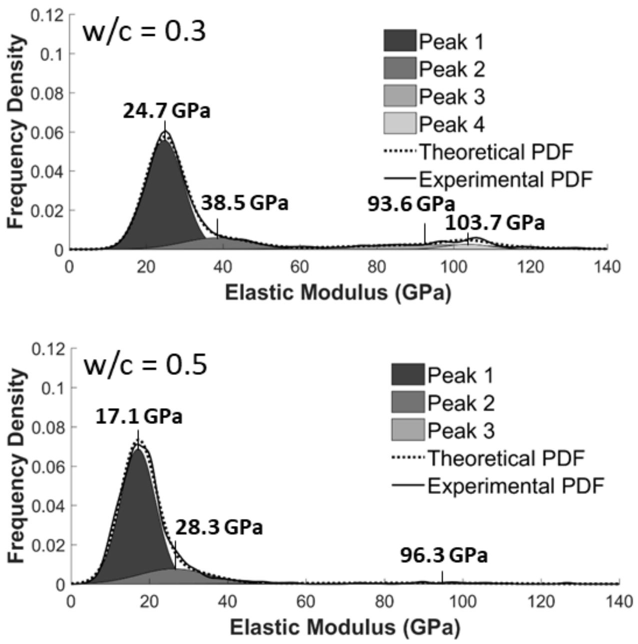
Nanoindentation and Micromechanical Characterization Mechanically Distinct Phases

HNC-free Cement Ink

3D Printed Filaments



Cast references



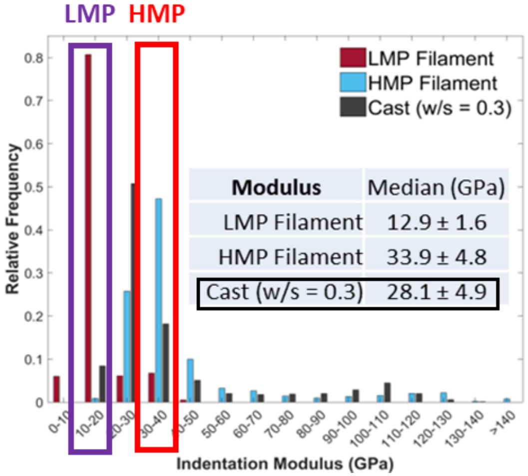
- Modulus distribution varies among printed filaments
- Higher w/c ratio correlates with lower modulus values
- Stiffness (modulus) of printed filaments affected by dynamic w/c ratio changes

HMP: High Mechanical Properties
LMP: Low Mechanical Properties

Kosson et al., JBE 66, 2023
https://doi.org/10.1016/j.jobe.2023.105874

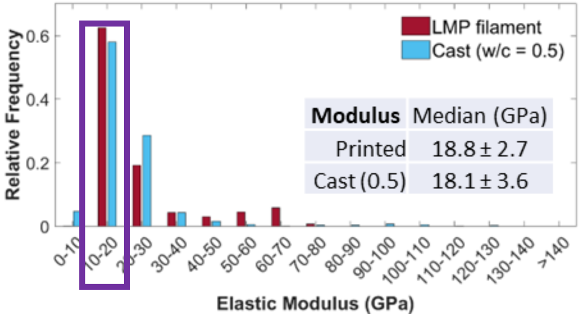
Nanoindentation and Micromechanical Characterization Mechanically Distinct Phases

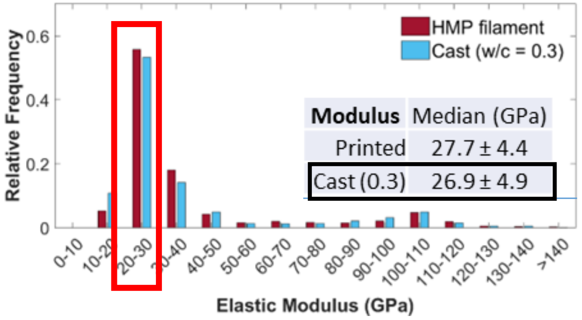
HNC Cement Ink



HNC-free Cement Ink

HMP: High Mechanical Properties
LMP: Low Mechanical Properties



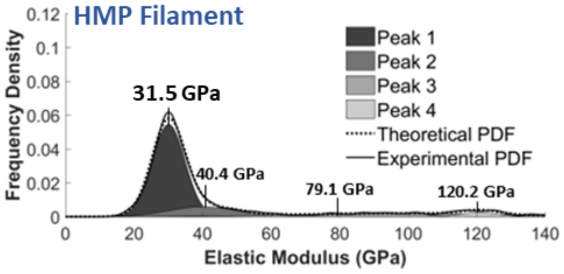


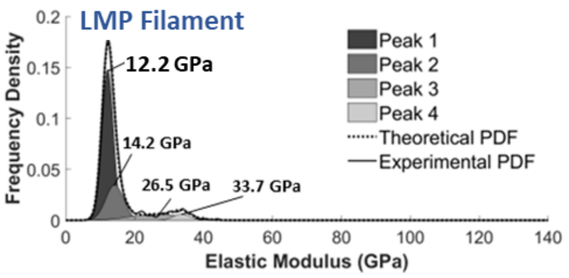
- HNC ink filament stiffness (modulus) varies, showing both higher and lower values compared to without
- HNC ink filaments showed HNC-induced strengthening
- HNC had no effect on the median modulus value of the cast specimens

Nanoindentation and Micromechanical Characterization Mechanically Distinct Phases

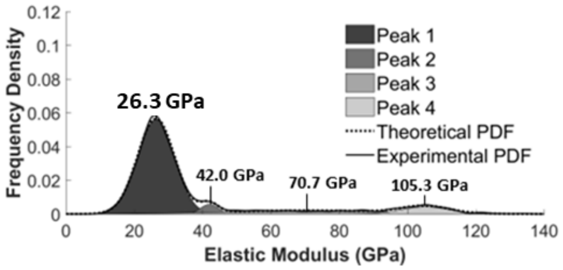
HNC Cement Ink

3D Printed Filaments





Cast (w/s = 0.3)



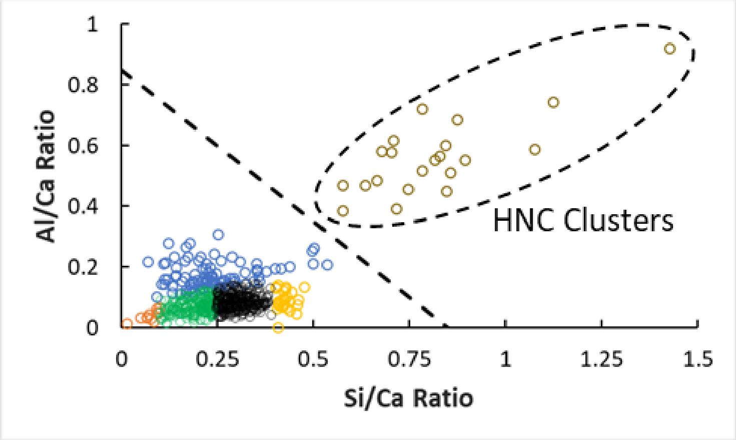
HMP: High Mechanical Properties
LMP: Low Mechanical Properties

Kosson et al., submitted

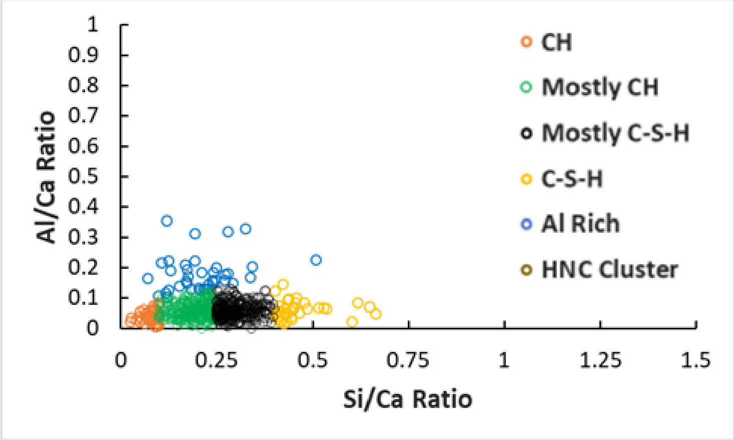
- Water segregation not the main factor
- HNC migration during extrusion influenced how stiffness was distributed among filaments
- Lower modulus values correlate with greater HNC clustering
- HMP filaments exhibited higher stiffness (modulus) than cast specimens

Nanoindentation and Micromechanical Characterization Chemical Signatures

HNC Ink Filament



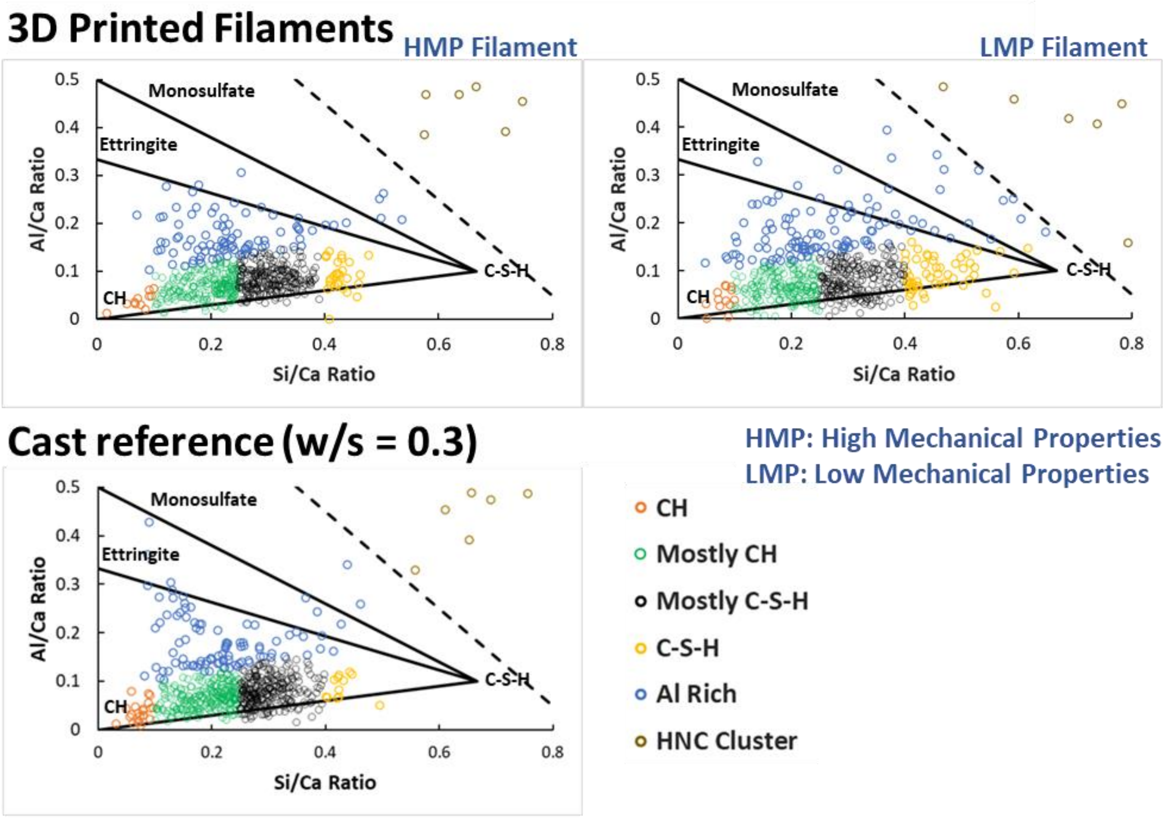
HNC-free Ink Filament



- High proportion of indents (>80%) associated with mixed C-S-H/CH phases
- Indents associated with HNC clusters show a diverse composition, indicating the presence of various hydration products within these clusters
- More Al-rich indents with HNC, indicating dispersed HNC fibers and aluminate phases

Nanoindentation and Micromechanical Characterization Chemical Signatures

HNC Cement Ink



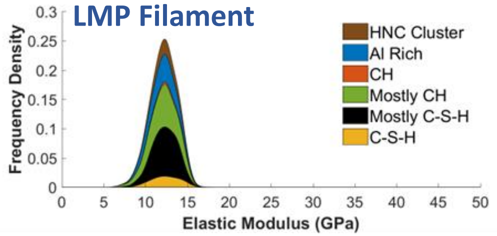
Kosson et al., submitted

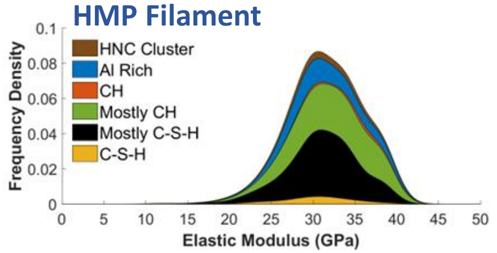
- More Al-rich indents for LMP filament
- Increased pozzolanic activity for LMP filament
- Highest concentration of dispersed HNC for LMP filament

Nanoindentation and Micromechanical Characterization Linking Chemical and Mechanical Information

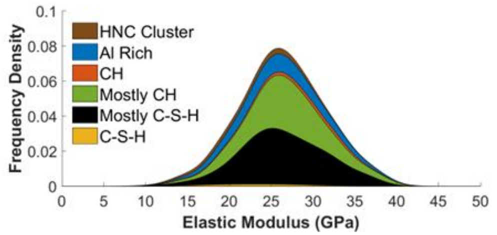
HNC Cement Ink

3D Printed Filaments



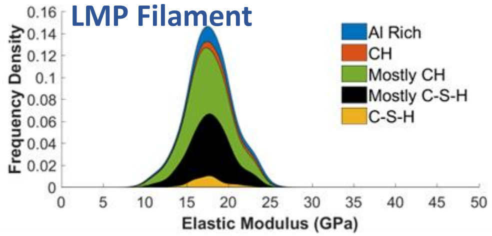


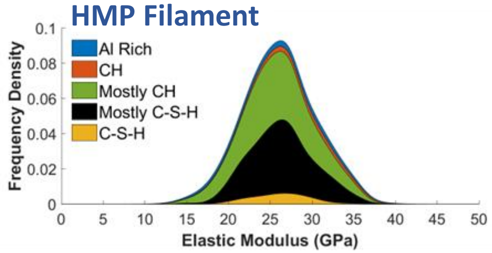
Cast reference (w/s = 0.3)

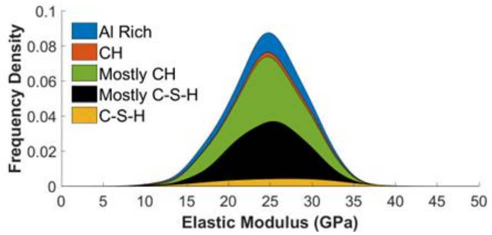


Kosson et al., submitted

HNC-free Cement Ink







Kosson et al., JBE 66, 2023
https://doi.org/10.1016/j.jobe.2023.105874

- Similar peak modulus values across the different hydrates within a given filament/cast specimen
- No dramatic changes in hydrate proportions within each ink
- Micromechanical differences attributed to changes in microstructural arrangement of hydrates, rather than changes in their proportions

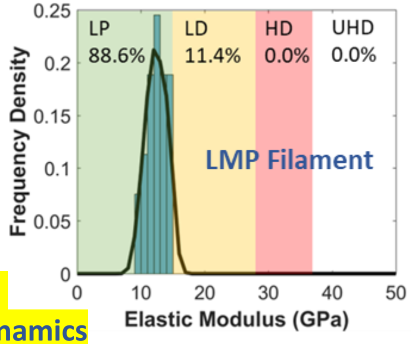
HMP: High Mechanical Properties
LMP: Low Mechanical Properties

Nanoindentation and Micromechanical Characterization C-S-H Phase Distribution

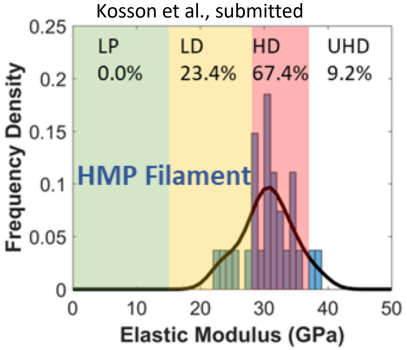
HNC Cement Ink

3D Printed Filaments

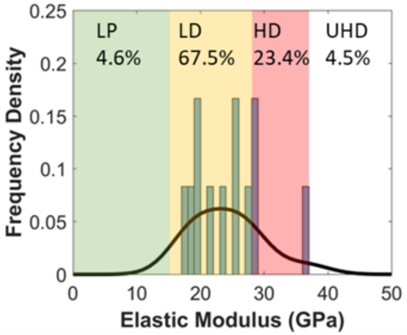
Effect of HNC clustering dynamics



Kosson et al., submitted



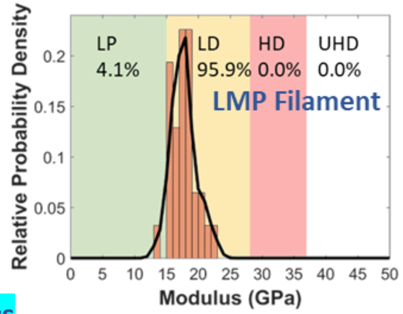
Cast (w/s = 0.3)



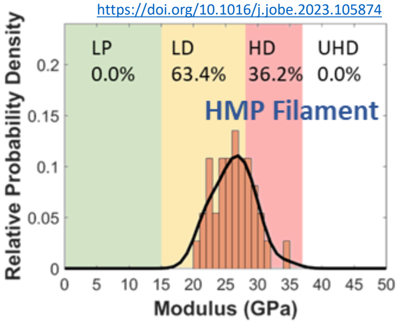
HNC-free Cement Ink

3D Printed Filaments

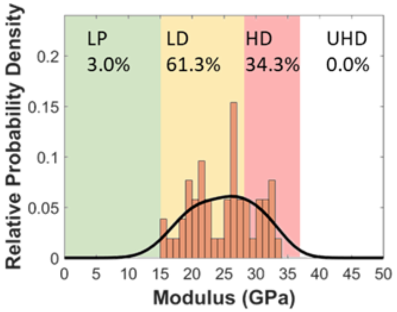
Effect of w/c ratio dynamics



Kosson et al., JBE 66, 2023
https://doi.org/10.1016/j.jobe.2023.105874



Cast (w/c = 0.3)



LP C-S-H (less than 15 GPa) LD C-S-H (15-28 GPa) HD C-S-H (28-37 GPa) UHD C-S-H (greater than 37 GPa)

HMP: High Mechanical Properties LMP: Low Mechanical Properties

- Small diameter extrusion influences C-S-H packing density
- C-S-H phases affected by local HNC concentration and clustering dynamics
- HNC concentration and dispersion affect C-S-H packing density
  - HMP: lower HNC concentration forms HD and UHD C-S-H
  - LMP: higher HNC concentration interrupts hydration matrix
  - Cast: higher degree of clustering

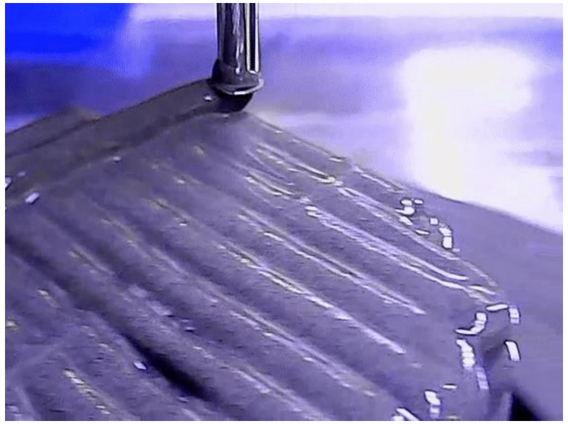
Conclusions

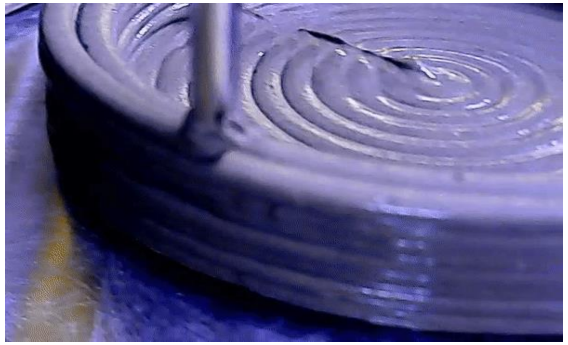
Small Filament Extrusion

- Impacts mesoscale hydrate assembly and micromechanical properties
- Leads to dynamic w/c ratio changes (without HNC)
- Induces dynamic shifts in HNC clustering and distribution

HNC Incorporation

- Enhances ink printability and limits extrusion-driven w/c changes
- HNC concentration in clustered and dispersed states affects the micromechanical properties and C-S-H packing density





M. Kosson and F. Sanchez, Vanderbilt, 2022

Acknowledgements

- National Science Foundation, NSF 1563389
- Vanderbilt University Discovery Grant
- Trans-Institution Program (TIP) Vanderbilt Reinvestment Award (VRA)

- Rossane Delapp – Senior Research Engineer
- Rich Teising – Staff Engineer

Multiscale Materials Performance Laboratory

Contact: florence.sanchez@Vanderbilt.edu
Learn more @
https://my.vanderbilt.edu/florencesanchez/