Rheological Control of 3D Printable Cement Paste and Mortars

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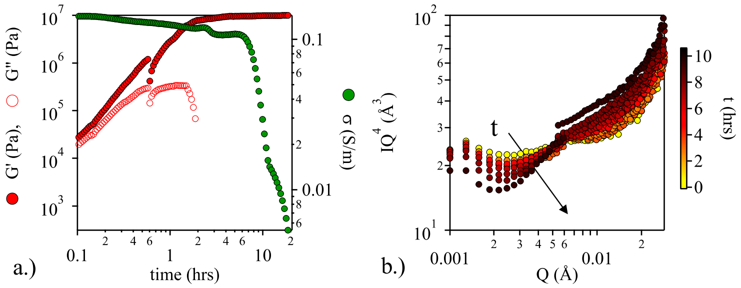
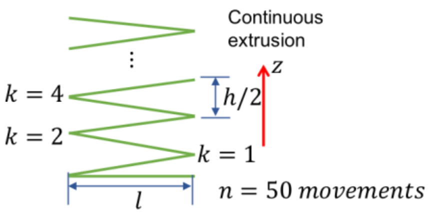
3-D Printing/Additive Manufacturing

Objective: Develop measurement science tools (*metrologies, standards,* and *guidance* documents) for quantitatively evaluating the critical material properties and ensuring the desired field performance of cement-based additive manufacturing.

How do we ensure a process or material is suitable for AM?





Measurement Science – Linking microstructure formation to macroscopic measurements

- Rheology and electrical conductivity are well known concrete test
- Small angle neutron scattering provides microstructure information

Standards Test Methods – Develop standard test methods for 3-D printing

- Verify Machine and material performance
- Compressive strength, slump, setting time, printability

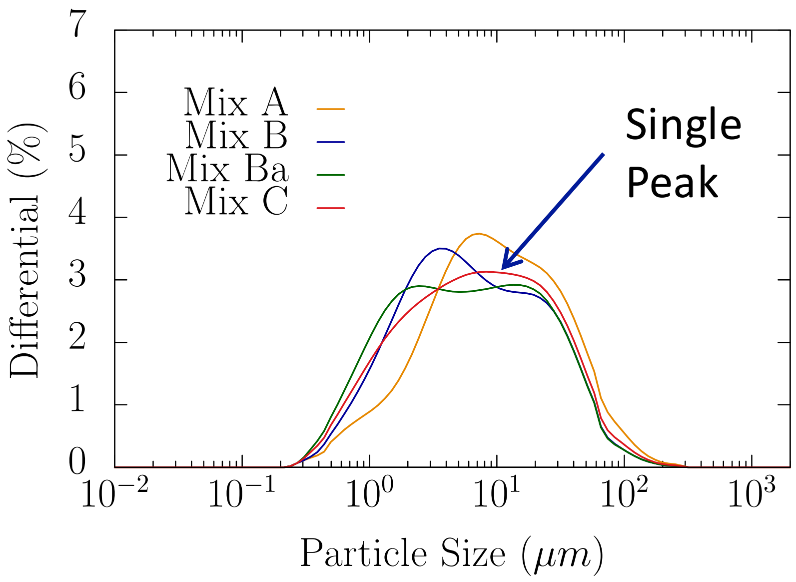
Technology Transfer – Form consortia to aid industry

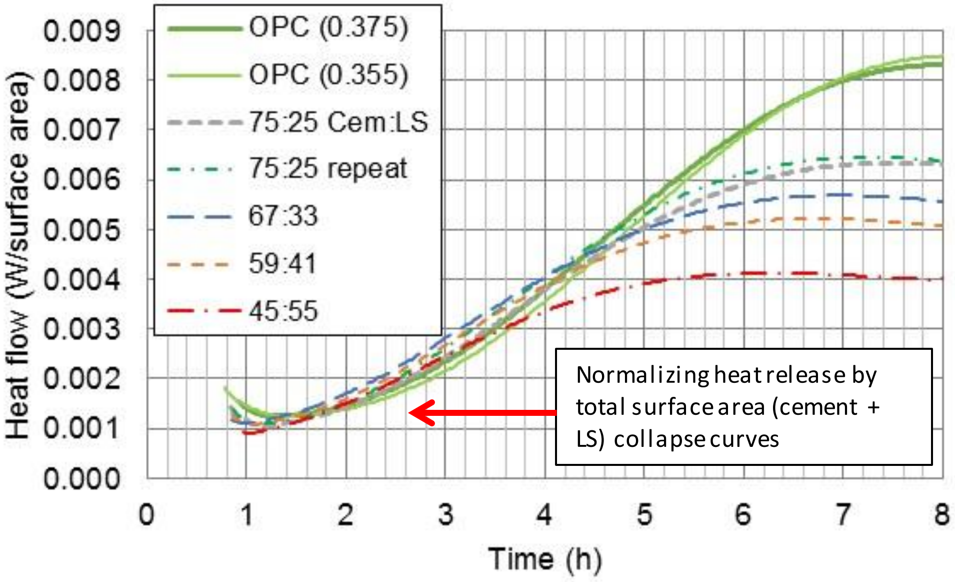
- Correlating off-line measurements to print quality
- In-situ and in-process measurements
- Hardened properties and scaling

Limestone Cements

- Print is possible during the first ~2 h after mixing
- Printed Mixtures = [dashed red box]
- Rheology during induction period controlled by availability of precipitation sites
- Mix B and C -> same surface area, increase D_{50}

	Mix A	Mix B	Mix Ba	Mix C
Limestone 1 ($kg\,m^{-3}$)	786.5	393.3	393.3	519.1 ↑
Limestone 2 ($kg\,m^{-3}$)	--	3933	--	--
Limestone 3 ($kg\,m^{-3}$)	--	--	393.3	267.4 ↓
Cement ($kg\,m^{-3}$)	786.5	786.5	786.5	786.5
Powder ($kg\,m^{-3}$)	1573.1	1573.1	1573.1	1573.1
Water ($kg\,m^{-3}$)	440.6	440.6	440.6	440.6
HRWRA ($mL\,kg_{cem}^{-1}$)	4	4	4	4
Water/powder	0.28	0.28	0.28	0.28
D_{50} (μm)	8.7	5.6	5.6	6.6
Surface area ($m^{-2}kg^{-1}$)	962.5	2357	3060	2389
Density ($kg\,m^{-3}$)	2014	2014	2014	2014
VF Water	0.44	0.44	0.44	0.44

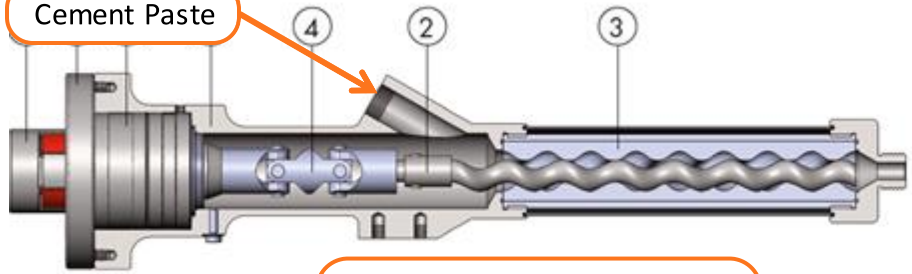




Cement Paste Printer

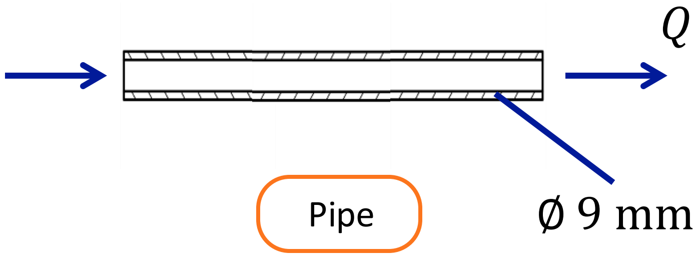
Pumping

Cement Paste



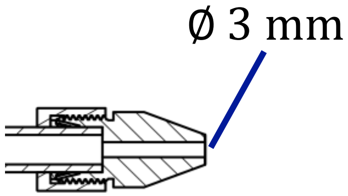
Progressive Cavity Pump

Pipe Flow

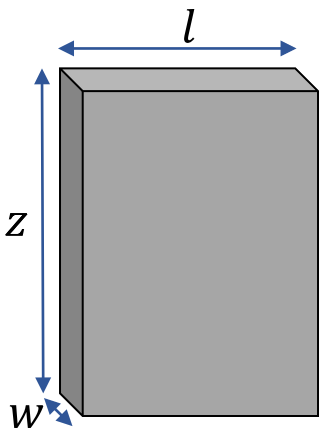


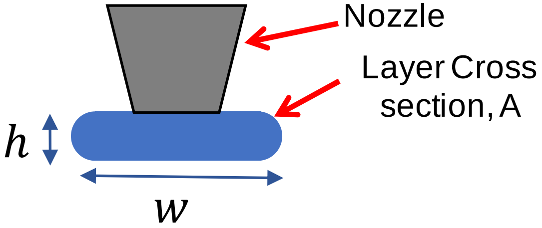
Pipe

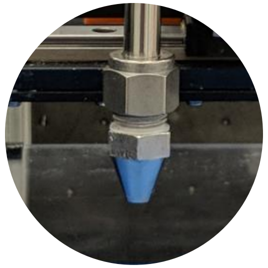
Deposition



Nozzle



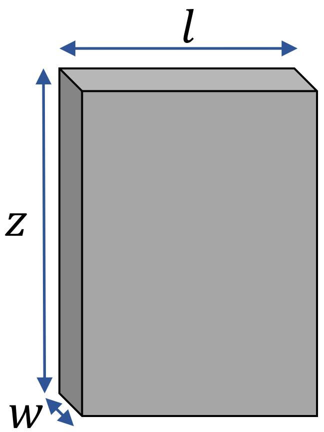


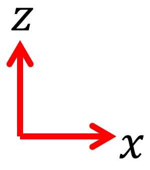


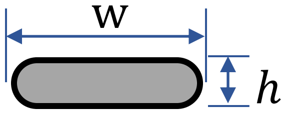
Testing material for "printability"

- The "printing" test should test material ability
  - Retain shape after deposition
  - Number of layers it can support
- Print quality is poor when…
  - Materials starts and stops flowing
  - Print speed is too fast
  - Nozzle diameter is too small or flow rate too fast.

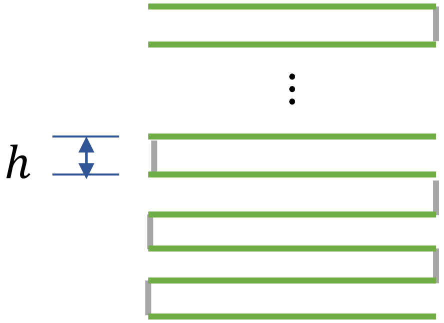
- Print quality is dependent on both material formulation and printing parameters
- Proposed test print – a tall, thin structure
  - Print 25 layers, h = 3 mm
  - Wall Width – 45 mm
  - Filament width – w = 4 mm
  - Flow rate – F = 13 mm^3/s



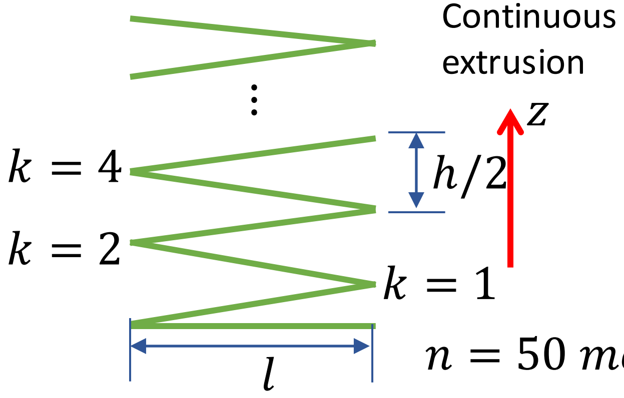




Filament
Cross section

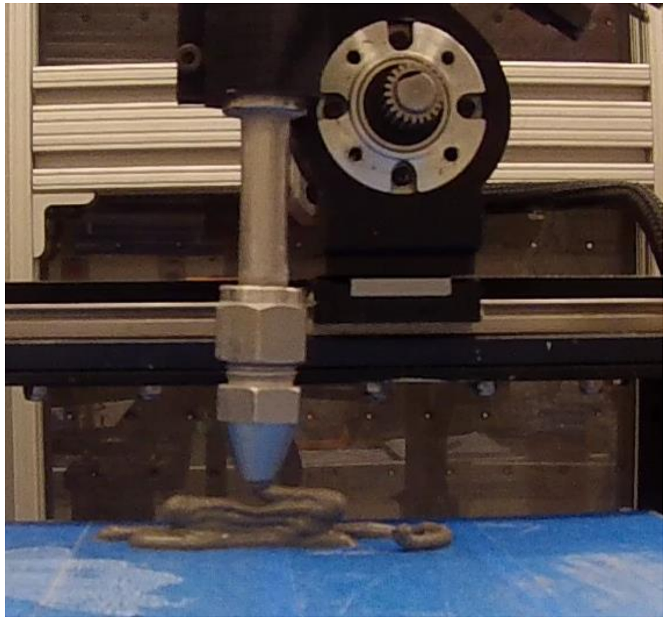


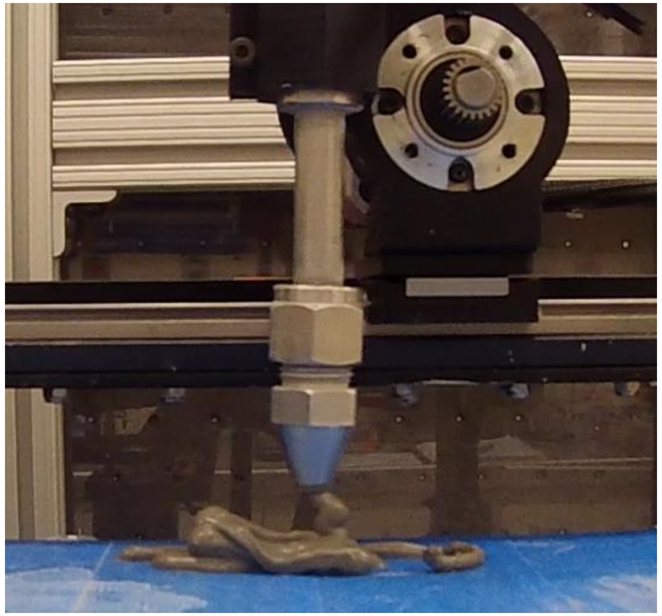
$n = 25$ *movements*



$n = 50$ *movements*

Printing Mix A

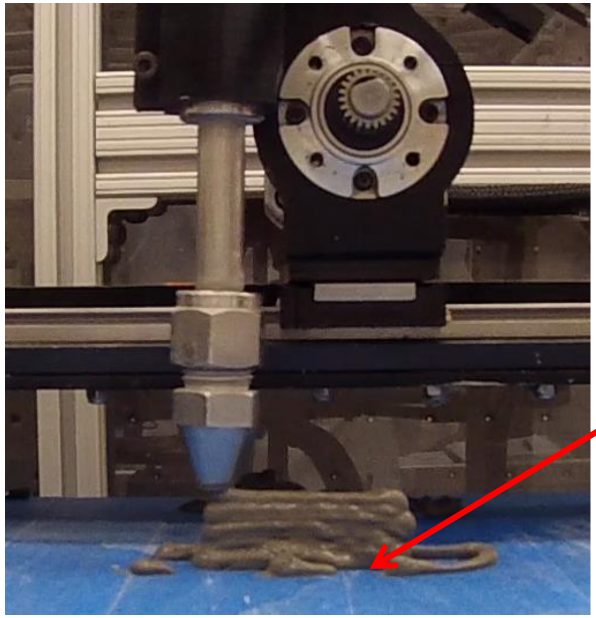




t = 50 min

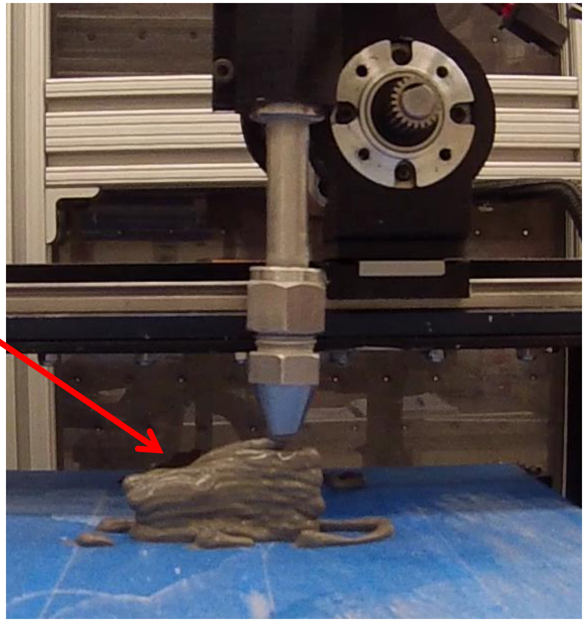
- First free standing structure
- Pumping – many air bubbles
- Printed 4 layers before collapse of first layer

Printing Mix A



Discontinuities resulting from poor pumping performance caused layer instability

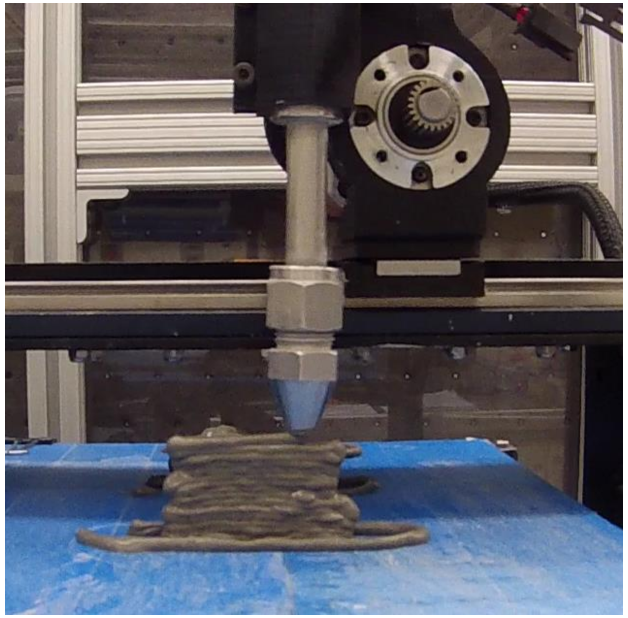
Pumping difficulties: air bubbles present in piping



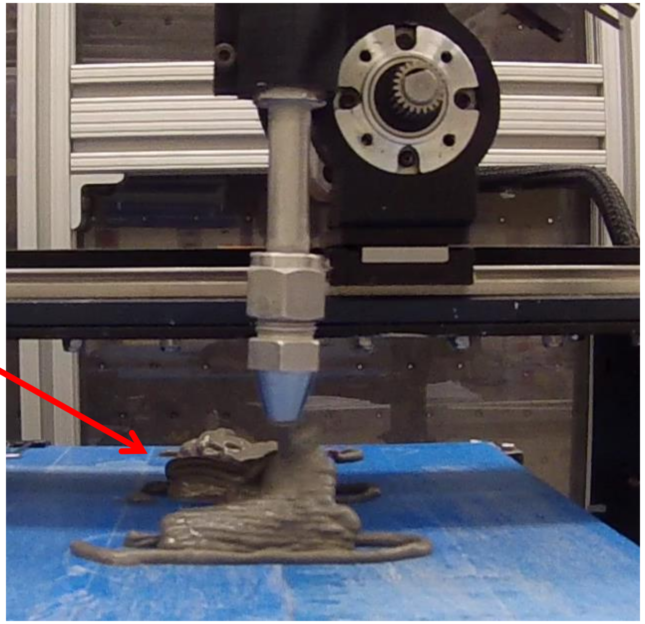
t = 60 min

- Pumping – many air bubbles
- Printed 6 layers before collapse of first layer
- Difficulty with start stop – indicated by discontinuous purge layer

Printing Mix A



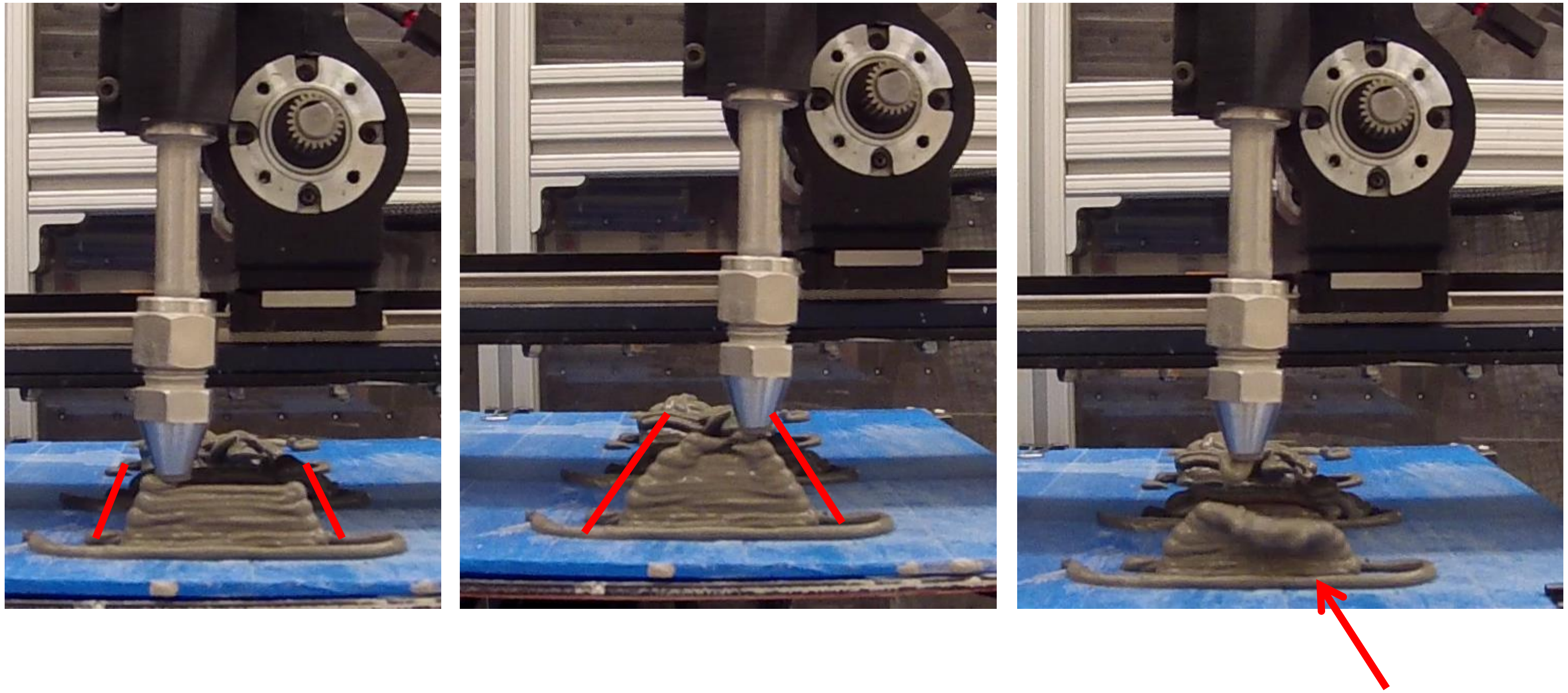
Collapse initiated at far end of structure – likely due do a void and instability due to nozzle movement



t = 65 min

- Pumping – many air bubbles
- Printed 9.5 layers before collapse of first layer
- Difficulty with start stop – indicated by discontinuous purge layer
- Collapse started at far end of structure

Printing Mix A

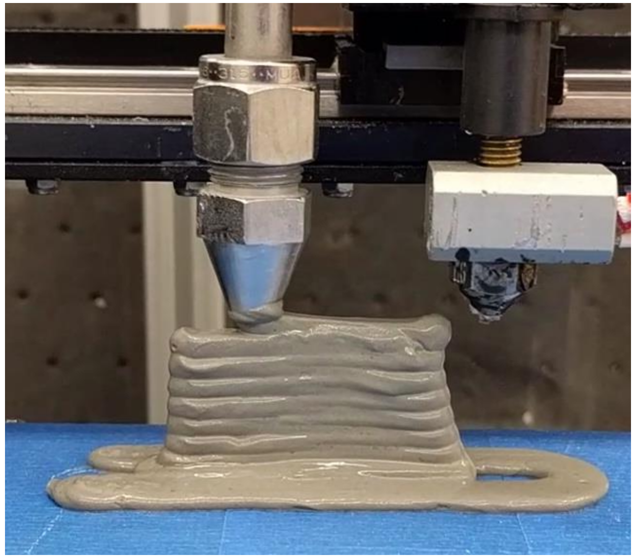
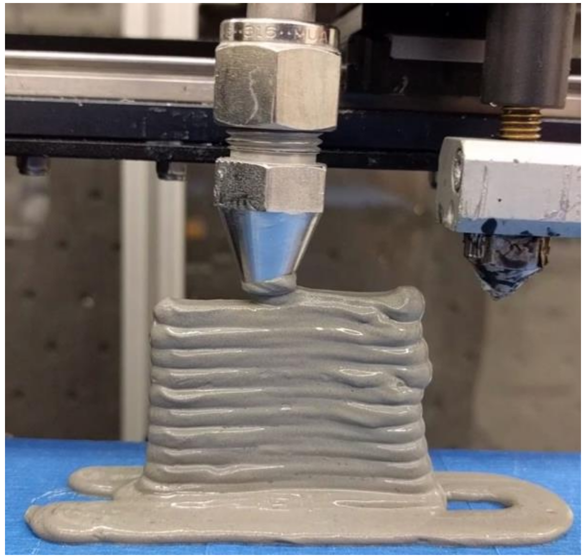
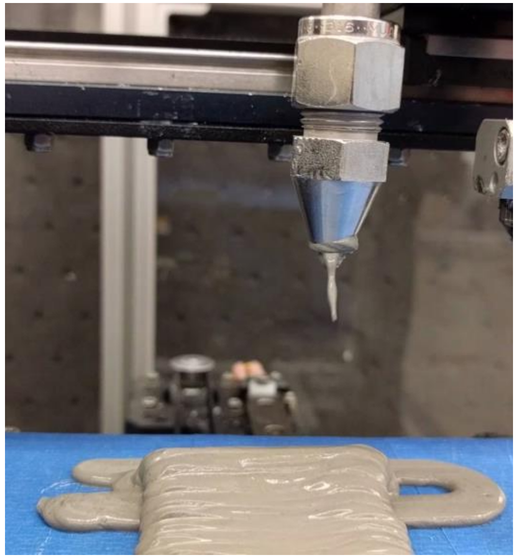


t = 70 min

Mass of material over small area overcame yield stress and caused collapse

- Pumping – many air bubbles
- Printed 7 layers before collapse of first layer
- Improved start stop performance
- Difficulty with “turns” – moving left to right, then right to left.
- Jamming in piping – not able to printer after this point

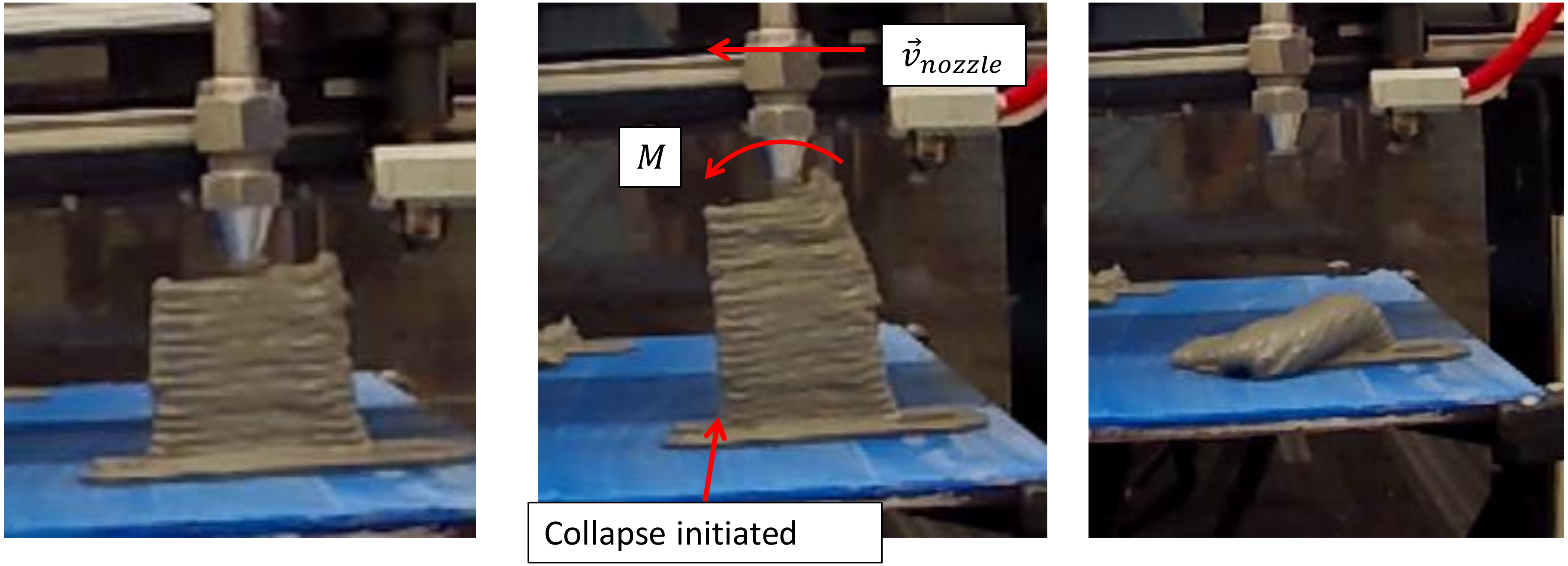
Printing Mix B

t = 30 min

- No pumping issues – no air bubbles
- Printed 15 layers before collapse of first layer
- First layer collapse

Printing Mix B

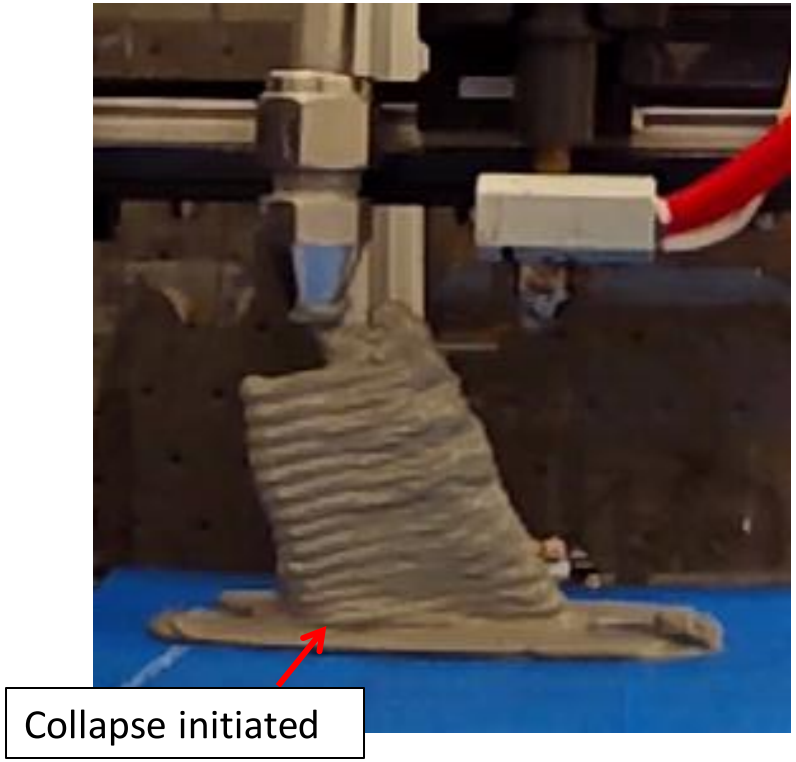


t = 40 min

- Printed 20 layers before collapse of first layer
- Material on nozzle pull column over
  - Nozzle moving to left
  - Material is attached to nozzle
  - This creates a bending moment which exceeds yield stress at collapse point

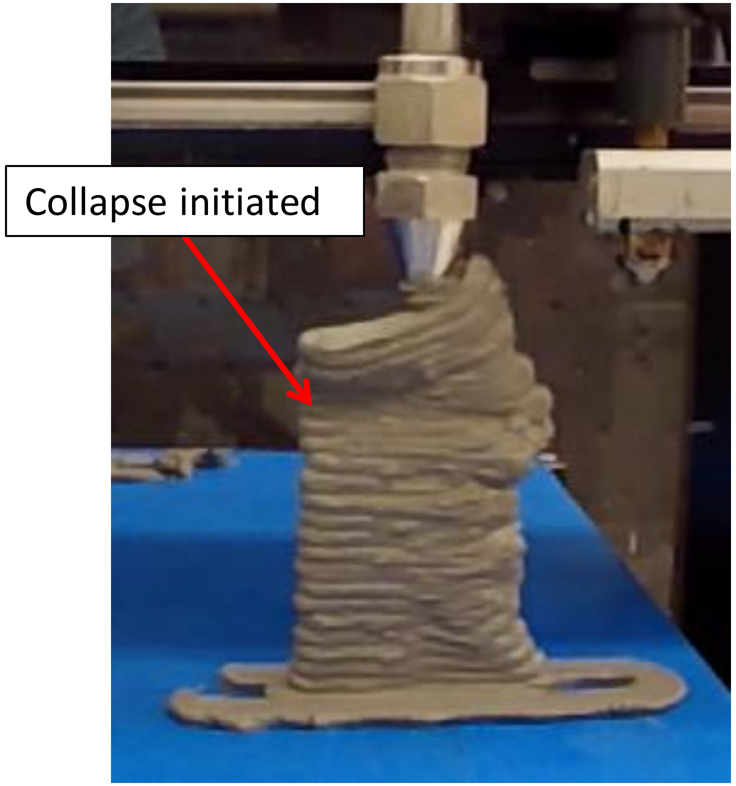
Printing Mix B

- Bending moment induced collapse observed for prints 3 and 4
- Collapse may also occur above bottom layer – at a defect



t = 47 min

- Printed 20 layers

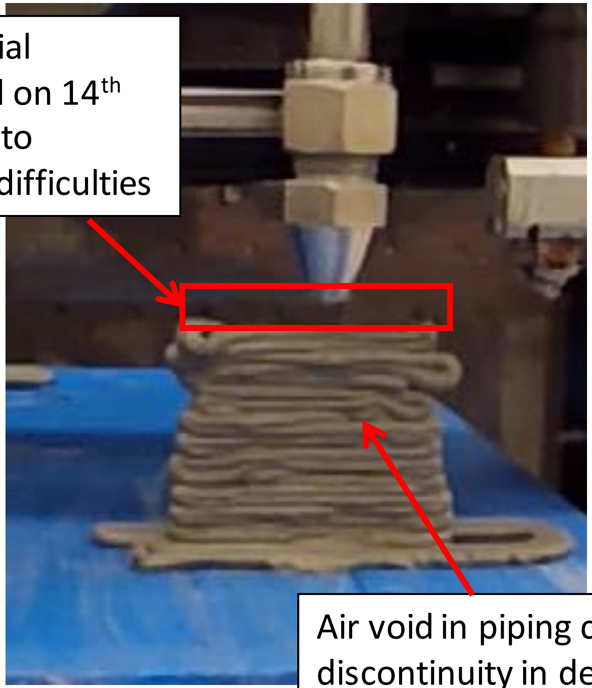


t = 53 min

- Printed 23 layers

Printing Mix B

- Similar collapse mechanisms occur for next two prints.
- Printing difficulties begin at 75 min with large voids forming in piping system



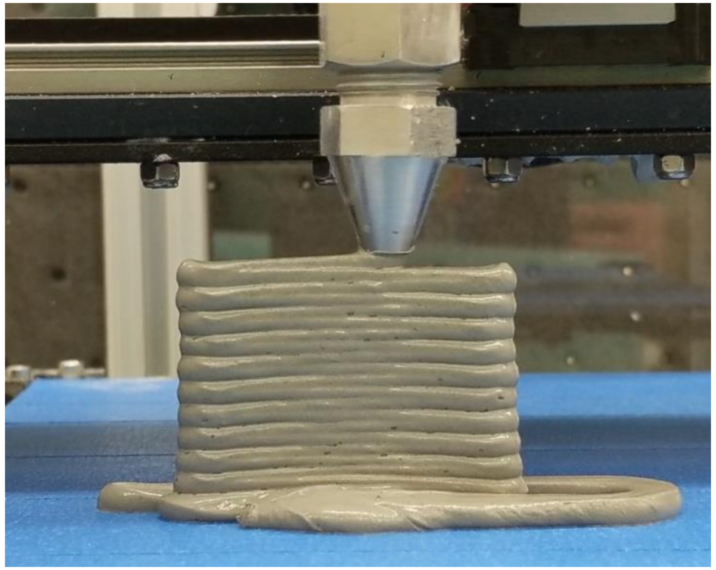
t = 75 min

- Print 9 layers before first void.
- Print 13 layers before first missing 14th layer

t = 80 min

- Pumping challenges caused several missed layers at beginning of print.

Printing Mix C

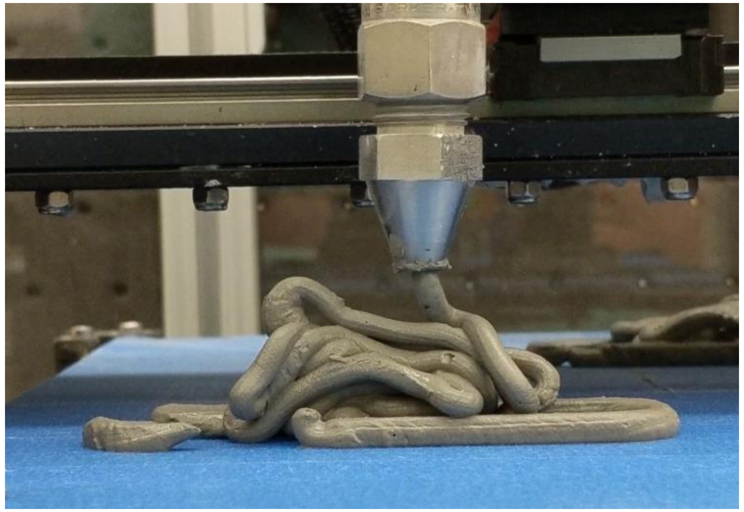


t = 12 min

13 layers

t = 53 min

24 layers



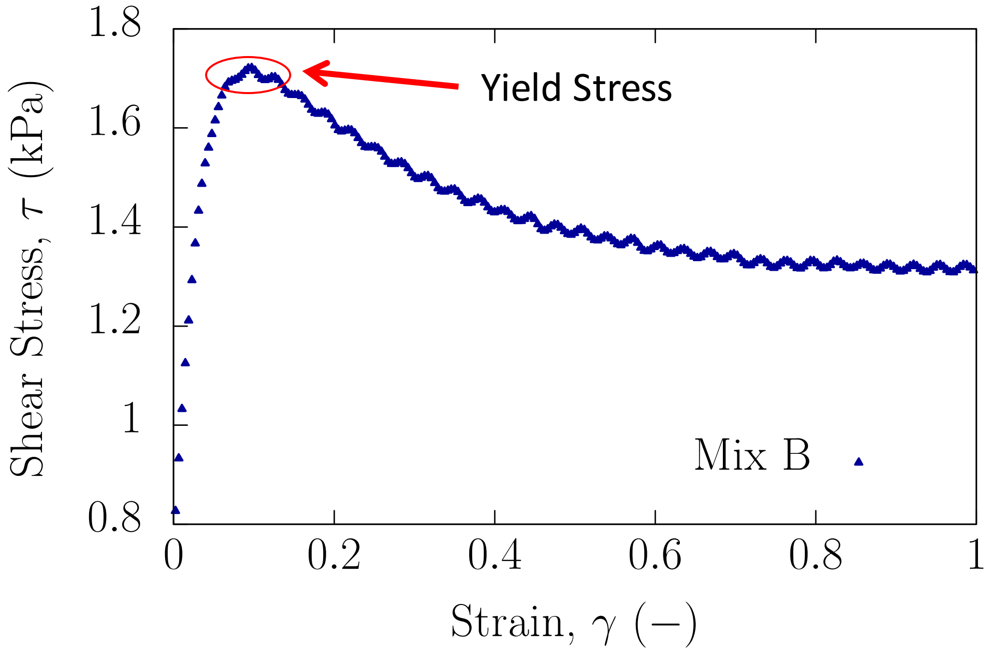
t = 71 min

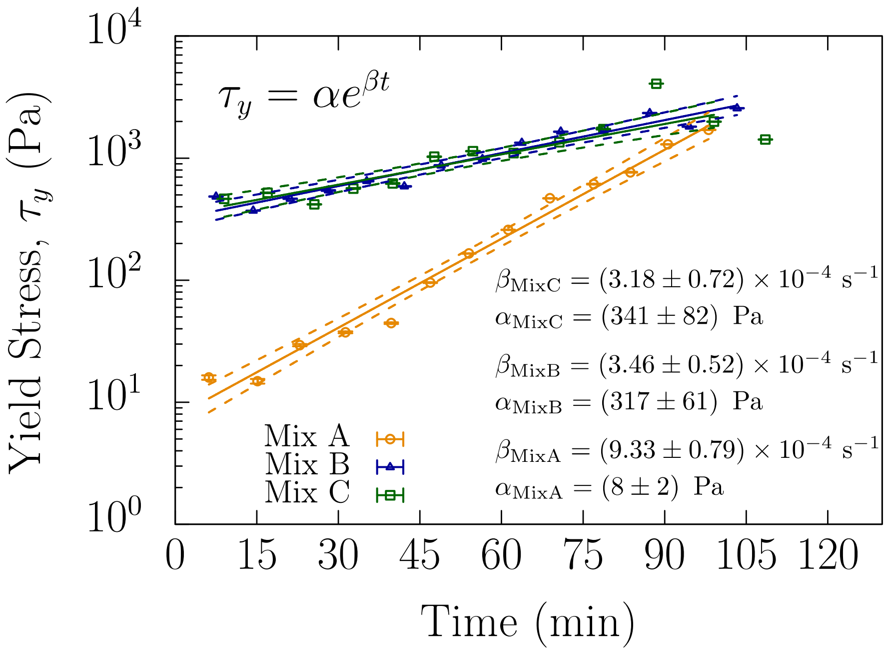
0 layers

Yield Stress

- Stiff materials difficult to test
  - Switch tool geometry to avoid slippage
- Yield Stress measurements made with a strain controlled rheometer
- Serrated 25 mm parallel plate
- Strain rate: $\dot{\gamma} = 1.0\ 1/s$

- Assess change in materials yield stress with time
- Two different material responses
- **Mix A:** low initial yield stress then rapid increase
- **Mix B:** high initial yield stress but steady increase
- **Mix C:** similar yield stress evolution to **Mix B**

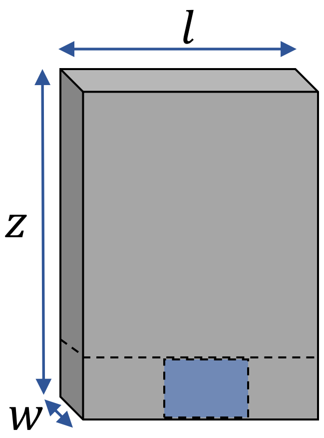




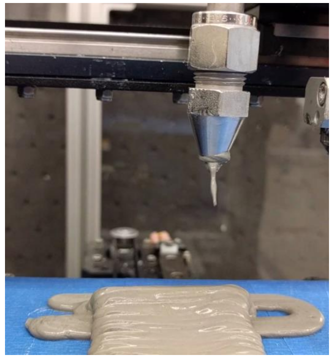
Analyzing Test

- Failure governed by first layer
- Yield stress as a function of time after mixing:

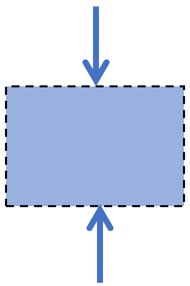
$$\tau_y(t) = \alpha e^{\beta t}$$

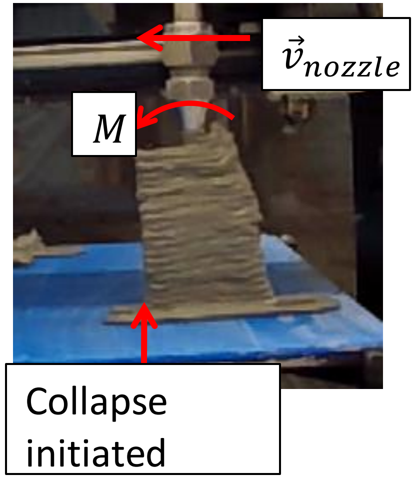


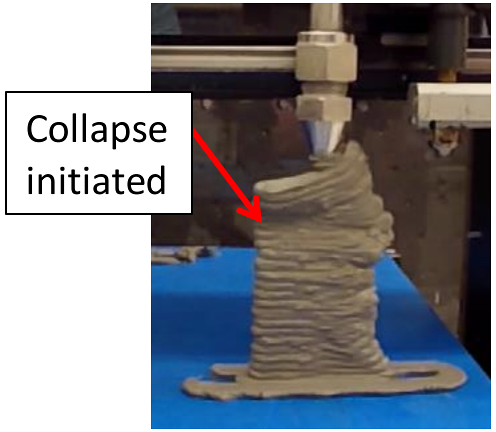
- Failure of structure changes and occurs before collapse of first layer



$$\sigma = k\rho_p g_0 h$$







- Tresca Failure Criterion:

$$\tau_y = \frac{1}{2}\sigma = \frac{1}{2}k\rho_p g_0 h$$

- Estimated time to first layer ($k = 1$):

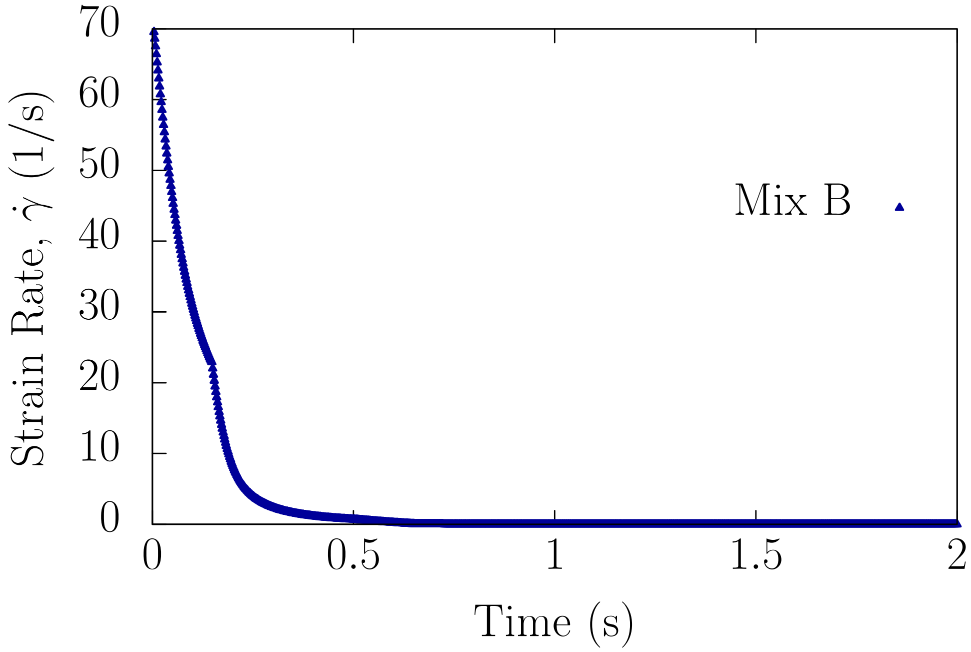
$$t_k = \frac{ln(\tau_y/\alpha)}{\beta} = \frac{ln\left(\frac{1/2\, k\rho_p g_0 h}{\alpha}\right)}{\beta}$$

	Calc. t_1	Meas. t_1
Mix A	11 min	50 min
Mix B	0 min	30 min

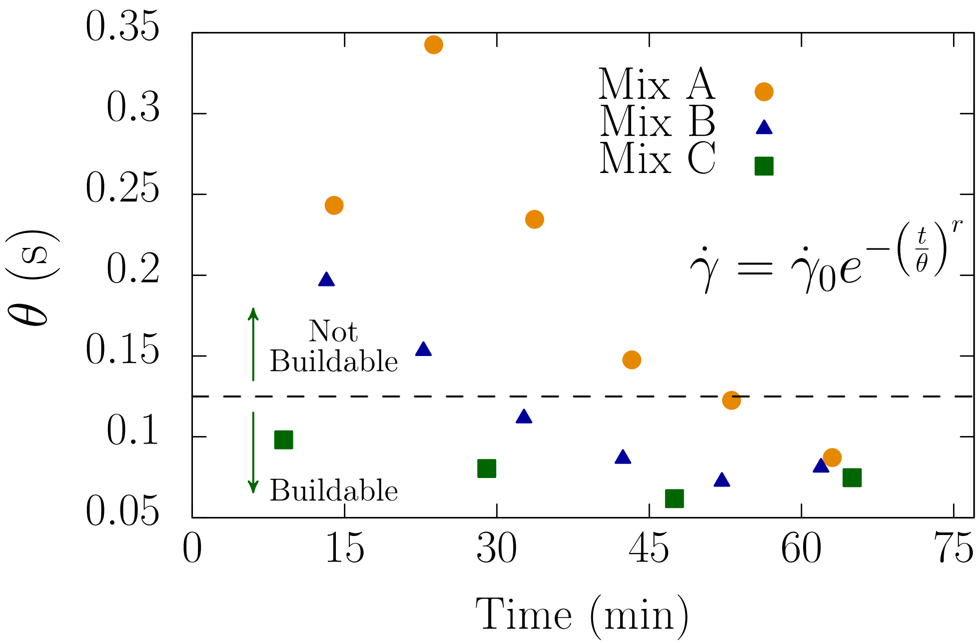
- As sample ages, failure transitions from failure of first layer to a buckling-like failure.
- Bucking failures are governed by geometry and elastic modulus.
- Can occur at stress below yield stress

Structure Rebuilding

- Rate at which material recovers yield stress
- Measure structural rebuilding by with stress controlled rheometer
  - Shear at 100 1/s for 60 s.
  - Apply stress to material – 10 % of measured yield stress – measure shear rate required to maintain stress level
  - Fit model to strain rate decay

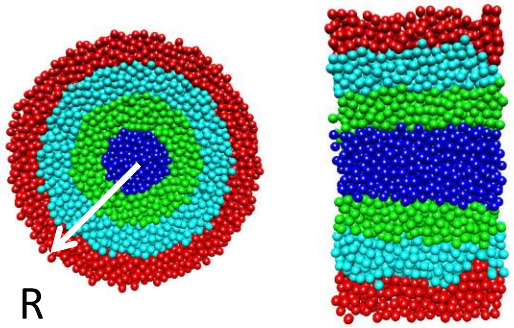


- **Mix B** recovered yield stress faster than **Mix A** for all times tested
- Beyond 67 min material began to slip in rheometer. For **Mix B** printing is possible up to 83 min.
- Below $\theta = 0.125\ s$, both Mix A and B are printable
- **Mix C** is printable from start

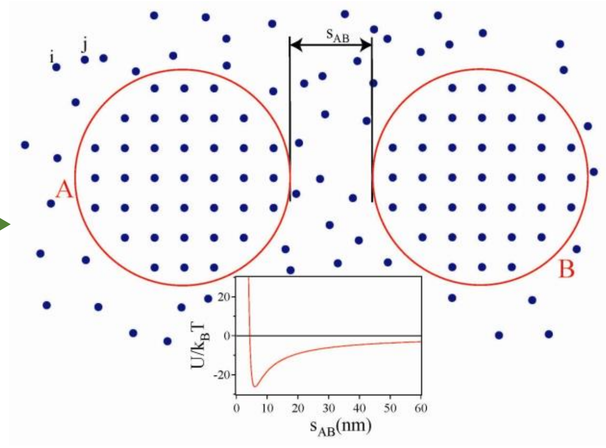


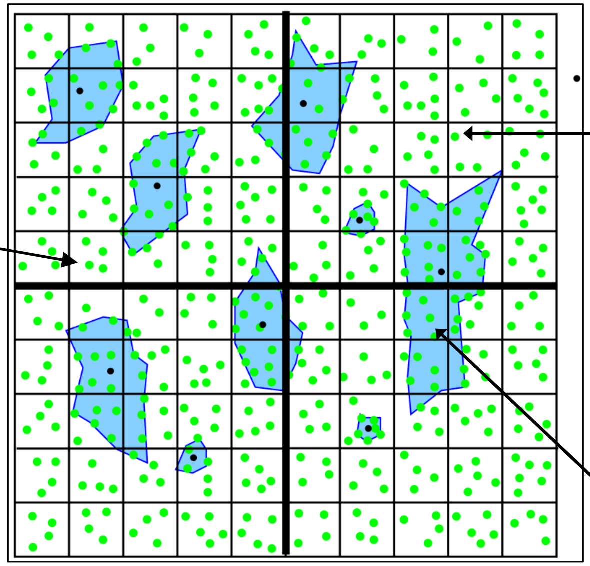
Kawashima et al. Cem. Concr. Res. (2013)

Scaling from Paste to Mortar: SPH Model



Particle-particle interactions





- Particles carry fluid properties

Velocity, Density

Temperature

Strain Rate

SPH interactions transfer momentum, density according to Gen. Navier Stokes equations

Rigid body represented by "freezing" a subset of particles and moving them according to the Euler equations.

- Lagrangian Formulation of Generalized Navier-Stokes Equation

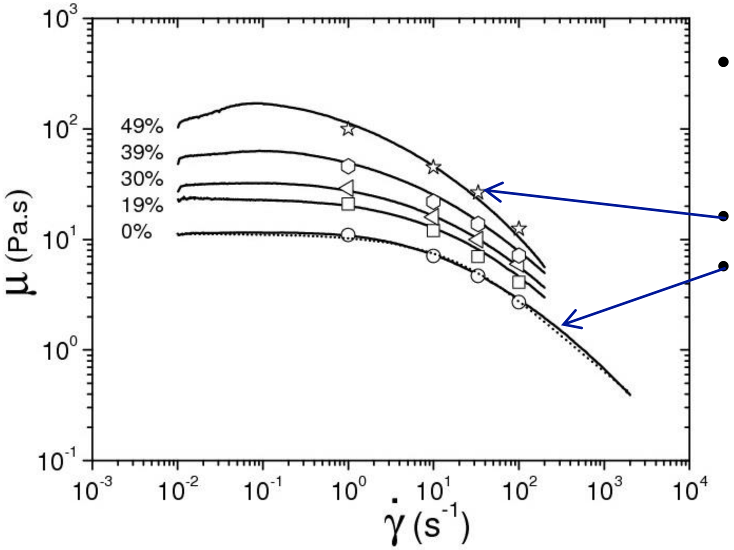
$$\rho \frac{\partial v}{\partial t} = \frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_k}\left[\mu\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\nabla\cdot v\right)\right] + \frac{\partial}{\partial x_i}(\zeta\nabla\cdot v)$$

- Lubrication Forces:

$$F_{LUB} \sim \frac{\mu(V_A - V_B)}{s_{AB}}$$

- Van der Waals Forces:

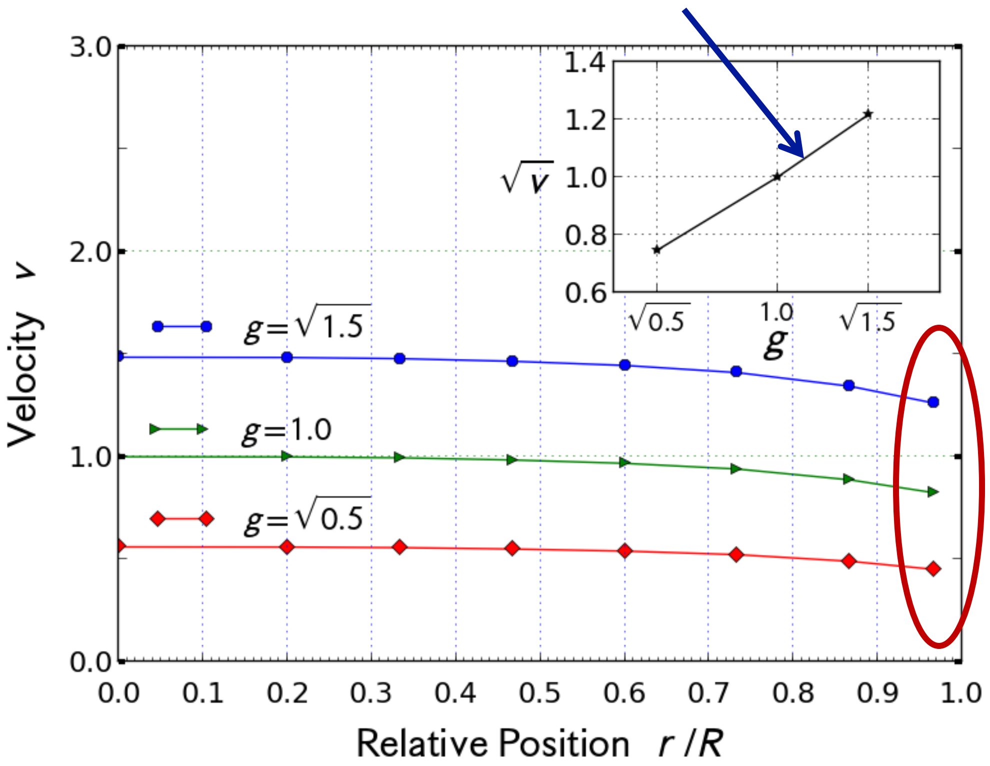
$$F_{INT} \sim \frac{H_{VAN}}{S_{AB}^2} + \frac{A_{HS}}{S_{AB}^8}$$



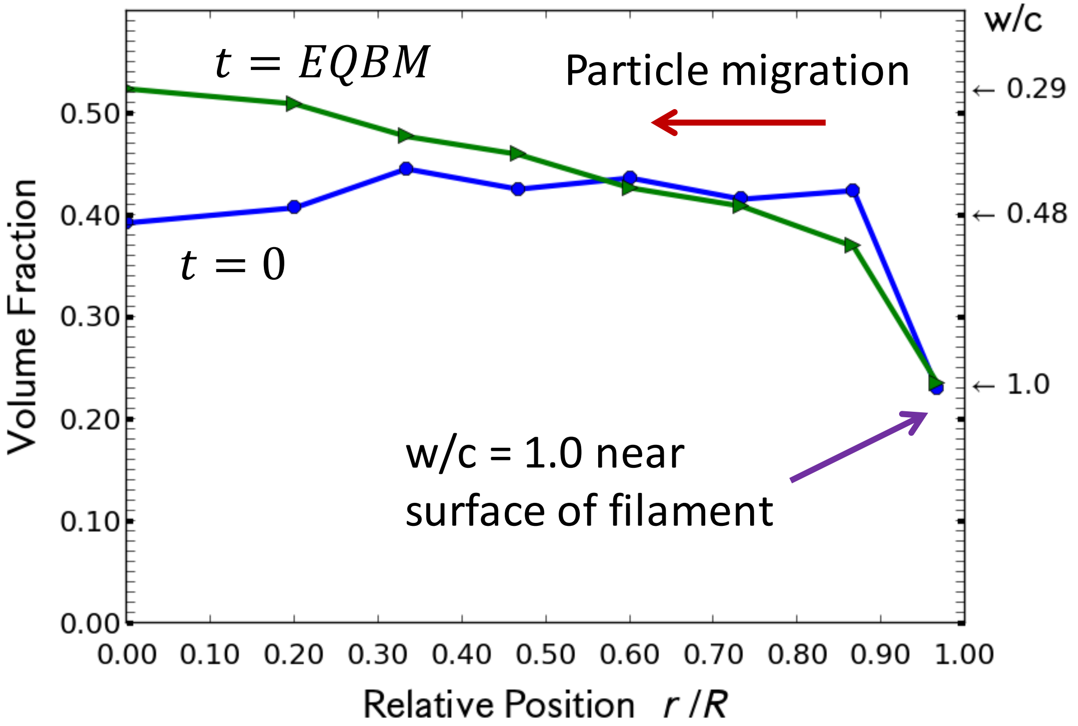
- Silica Spheres in 5 % Methylhydroxypropyl - cellulose in water
- Experimental measurements
- Simulation results

SPH Model: Flow in a Pipe

- Preliminary Simulations: w/c = 0.48, 1 mm sand in Ø3 cm pipe
- Matrix fluid assumed power-law behavior of $n = \frac{1}{2}$
- $\Delta P = g$ across length of pipe in simulation
- Changing applied pressure, $V \sim g^{1/n}$
  - Flow rage scales proportional to g^2



- Locally high shear rates produce lubrication layer
  - Fully developed flow
  - $n = 0$ → plug flow; $n = \frac{3}{2}$ → Shear thickening
- Shear induced particle migration: particles flow toward center of pipe, altering w/c. Occurs within 4 to 5 pipe diameters.



Lab to Commercialization

- Continue studies to understand relationship between material properties, machine settings, print quality, and print performance.
  - Control onset of initial set.
  - Material delivery.
- Codes and Standards
  - Measuring compressive strength, rheology, and other material properties.
  - Performance-based specification of materials!
- In-line and in-situ measurements of material properties – NDT/NDE
  - Cold joint and flaw detection.
  - Strength build up.
- Machine design
  - Nozzle design – influence on print quality.
- What about reinforcements?
  - Fibers – orientation and effectiveness.
  - Parallel printing – incorporate other AM techniques to create reinforcement.
- Consortium: Metrology of Additive Construction by Extrusion (MACE)
  - Partnership between government, industry, and academia

Working with NIST

Metrology of Additive Construction by Extrusion

Objective will be achieved by identifying and then translating cementitious material measurements to in-line or in-process measurements for quality assurance and success of the Additive Construction by Extrusion process.

Part 1: Correlating off-line Measurements to Print Quality

Part 2: In-situ and In-process Measurements

Part 3: Hardened Prosperities and Scaling up to Concrete

Now accepting members!

Interested? Contact:

Scott Jones at scott.jones@nist.gov

NIST NRC Postdoctoral Research Associateships Program

Microstructural Modeling of Cement-based Materials

Adviser: Jeffrey W. Bullard (Jeffrey.bullard@nist.gov)

Rheological Measurements of Cementitious Materials

Adviser: Nick Martys (nicos.martys@nist.gov)

2,048 — Number of NIST NRC **postdocs** since 1955

33% — NIST NRC postdocs from 1990-2013 became NIST **employees**

68% — NIST **PECASE* award winners** between 1998-2014 have been NRC postdocs

Data current as of October 2017

** Presidential Early Career Awards for Scientists and Engineers*

Thank You!

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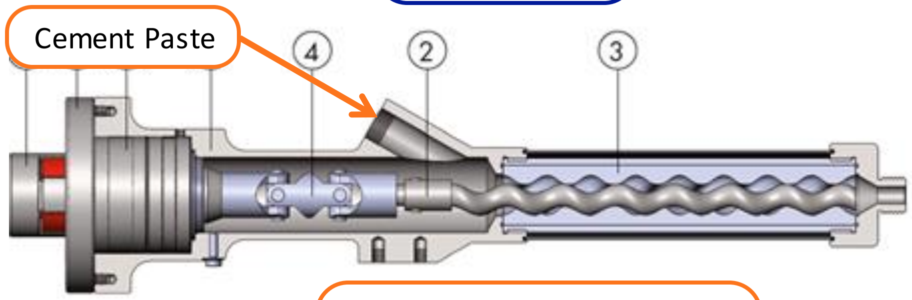
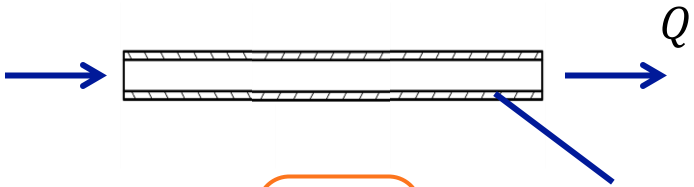
Cement Paste Printer

Pumping



Progressive Cavity Pump

Pipe Flow

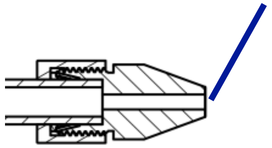


Pipe

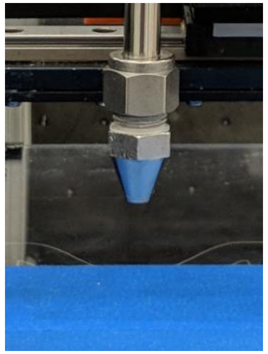
Ø 9 mm

Deposition

Ø 3 mm



Nozzle



Estimated Shear rate

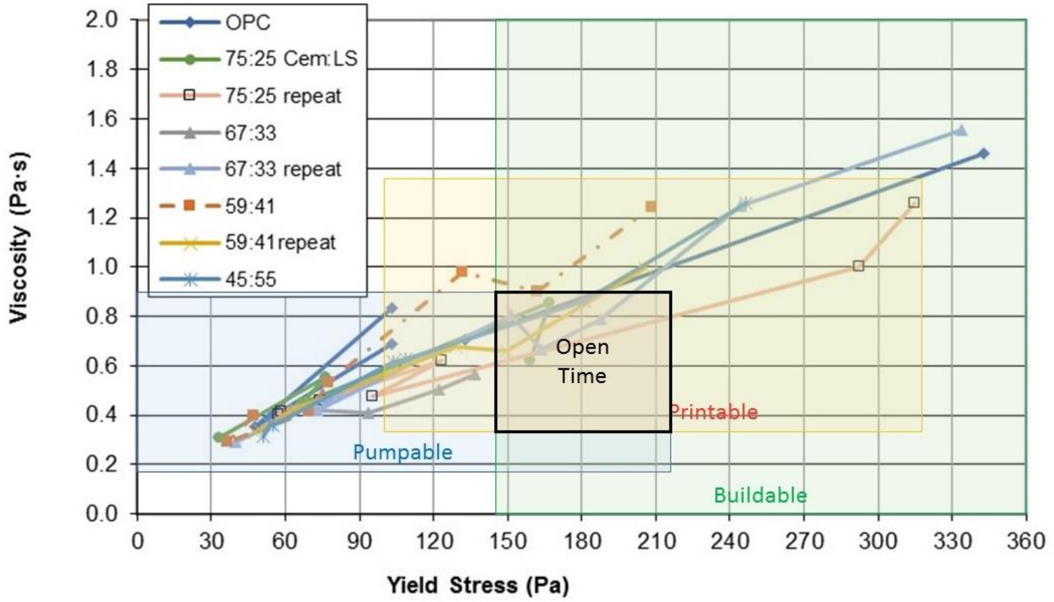
$$\dot{\gamma} = \frac{4Q}{\pi r^3}$$

Flow Rate = 13 $\mathrm{mm^3 s^{-1}}$

$$\dot{\gamma}_{pipe} = 4\ \mathrm{s^{-1}}$$

$$\dot{\gamma}_{nozzle} = 11\ \mathrm{s^{-1}}$$

Relating Rheology to Printing



Evaluate material material performance:

- **Pumpability** - The ease and reliability with which material is moved through the delivery system
- **Printability** - The ease and reliability of depositing material through a deposition device
- **Buildability** - The resistance of deposited wet material to deformation under load
- **Open Time** - The period where the above properties are consistent within acceptable tolerances

References:
Lim et al. Automation in Construction (2012) 21:262–268
Le et al. Materials and Structures (2012) 45:1221–1232

Control material rheology:

- Limestone powder additions
  - Cement:Limestone - 67:33, 80:20, 50:25:25 by mass
- Control hydration kinetics
  - Slow hydration – sodium gluconate and sucrose: 1 - 2 µL/g-powder
  - Accelerate hydration – Aluminum sulfate: 0.03 g/g-paste (3 %)

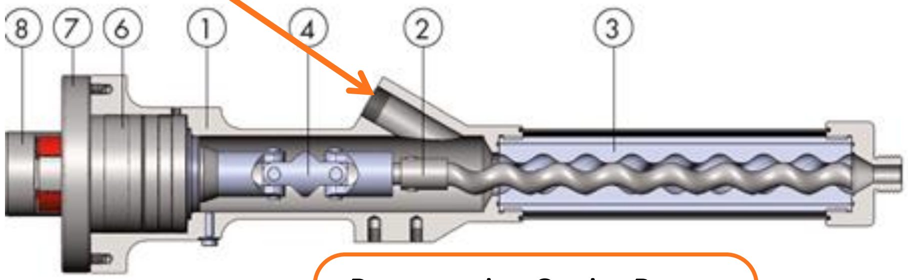
Rheology Measurements:

- Yield stress and viscosity using parallel plate geometry
- Mini-slump measurements

Cement Paste Printer

Pumping

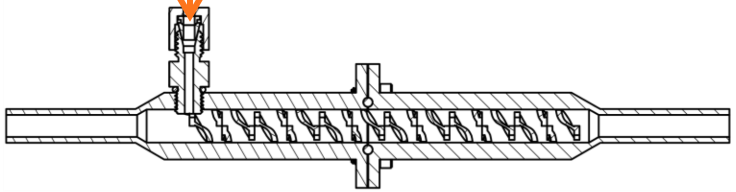
Cement Paste



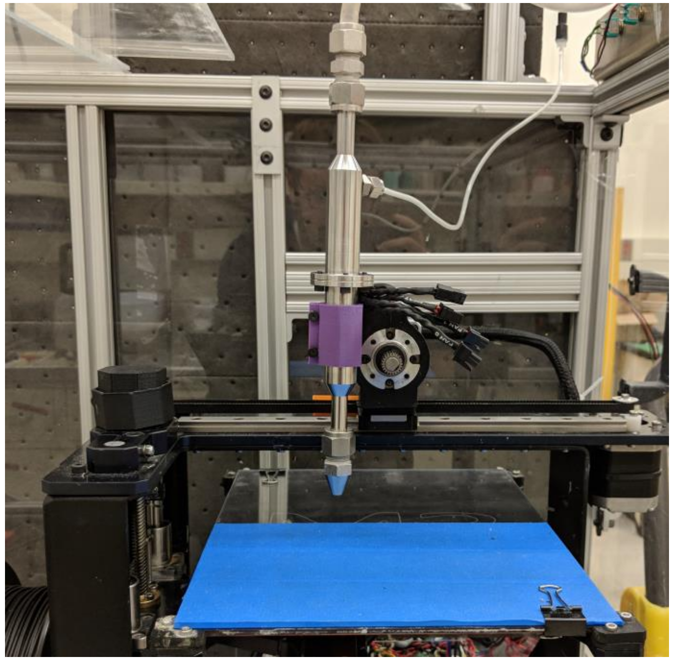
Progressive Cavity Pump

Mixing

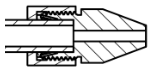
Set Accelerator



Static Mixer

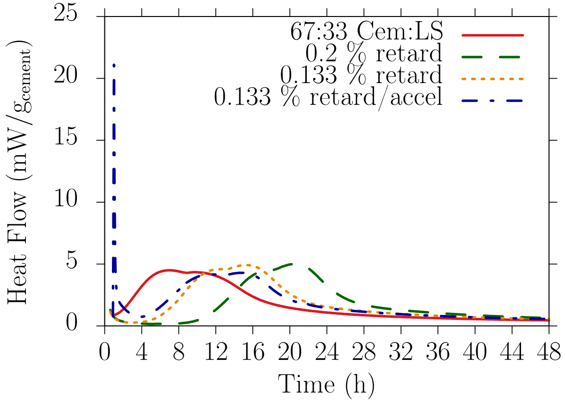


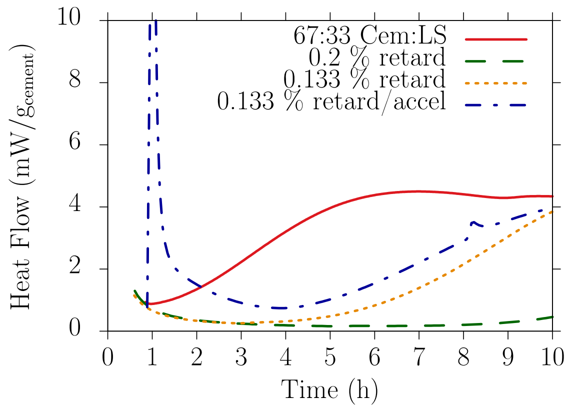
Dispensing

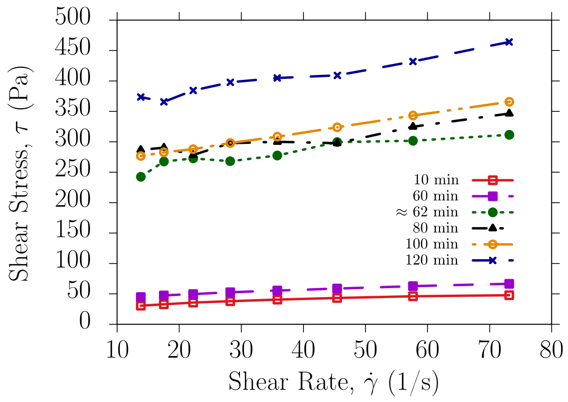


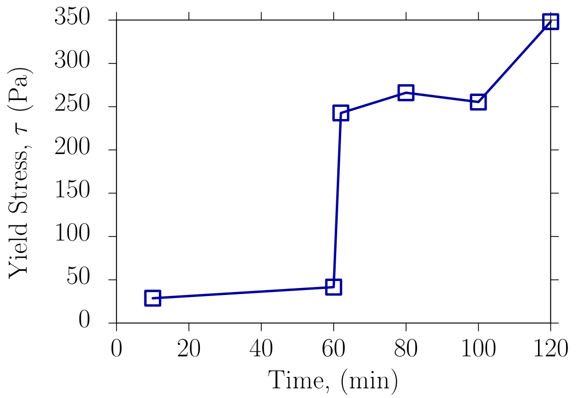
Nozzle

Increase Working Time with Admixtures







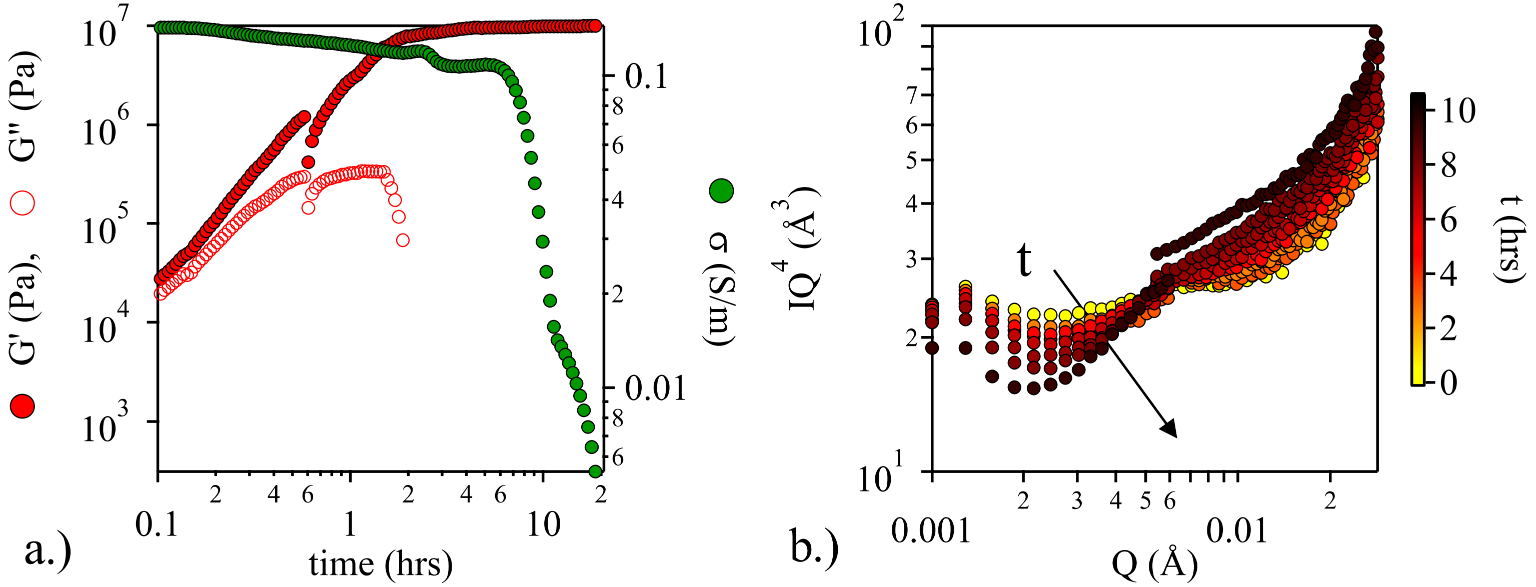


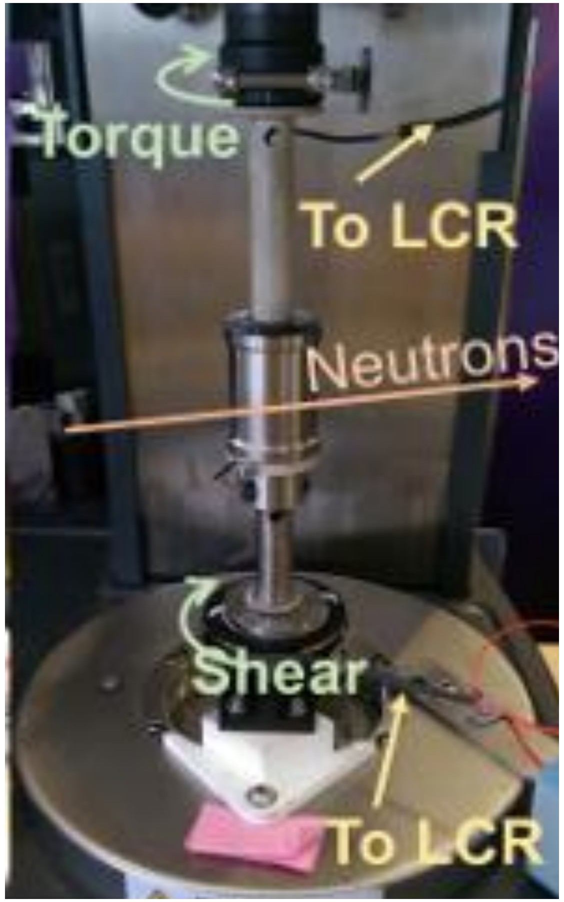
- Retarder dosage of 1.33 µL/g-powder produced 5 h dormant period
- Initial spike due to mixing and, possibly, ettringite formation
- Beyond dormant period, hydration is controlled by water content and particle size of powder

Without remixing, hydration products continue to form, increasing yield stress

- Injection of accelerator causes initial increase in yield stress likely due to ettringite formation
- Remixing breaks down the structure causing a drop in yield stress
- However, without remixing, hydration product formation causes continuous increase in yield stress

Dielectric RheoSANS





https://dx.doi.org/10.3791/55318

- Rheology, conductivity, and Neutron scattering in parallel measurements
  - SAOS/LAOS
- Linking structure formation to rheology and conductivity measurements
- Study effect of hydration retarders and accelerators on structure formation