Dipartimento di
Ingegneria Industriale

Direct and indirect 3D printing with geopolymers

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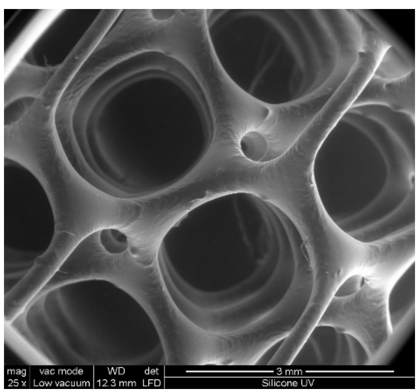
Advanced Ceramics and Glasses

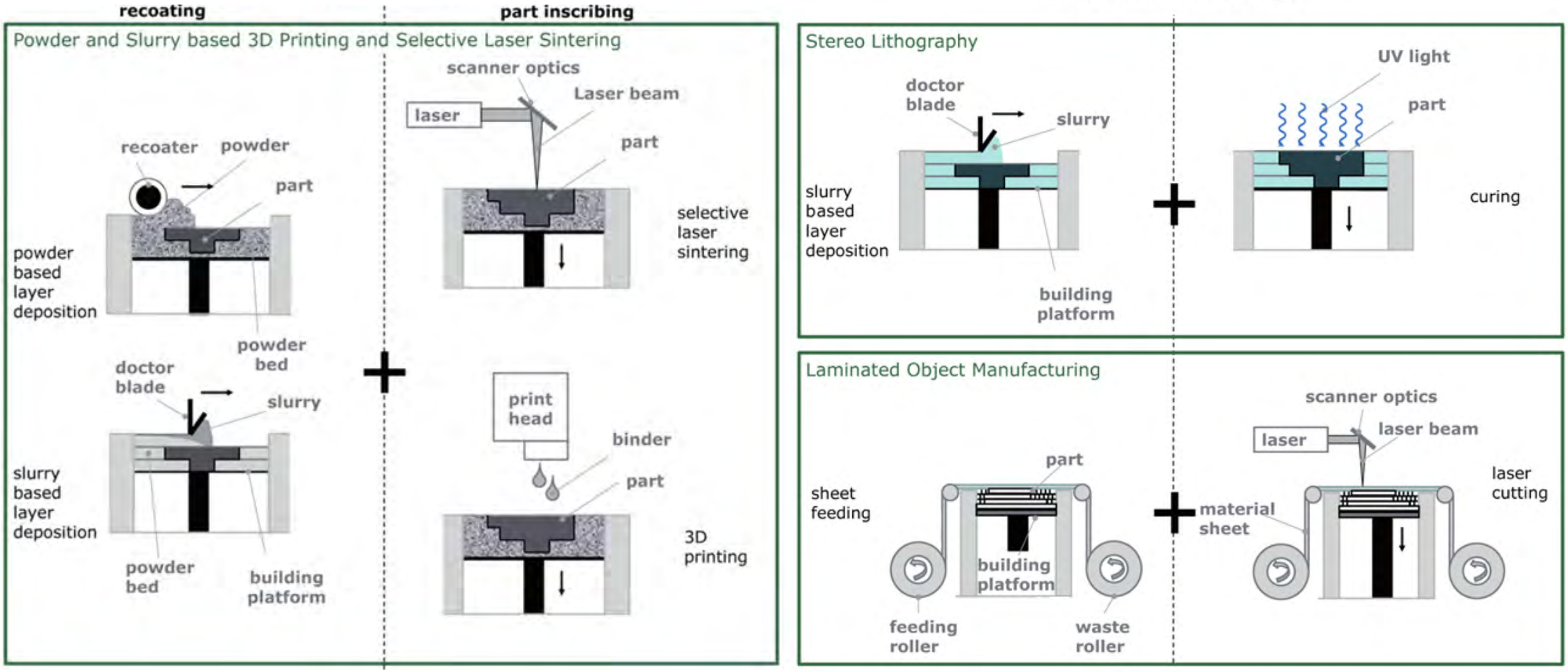
Heads: Prof. Paolo Colombo and Prof. Enrico Bernardo



Research topics:

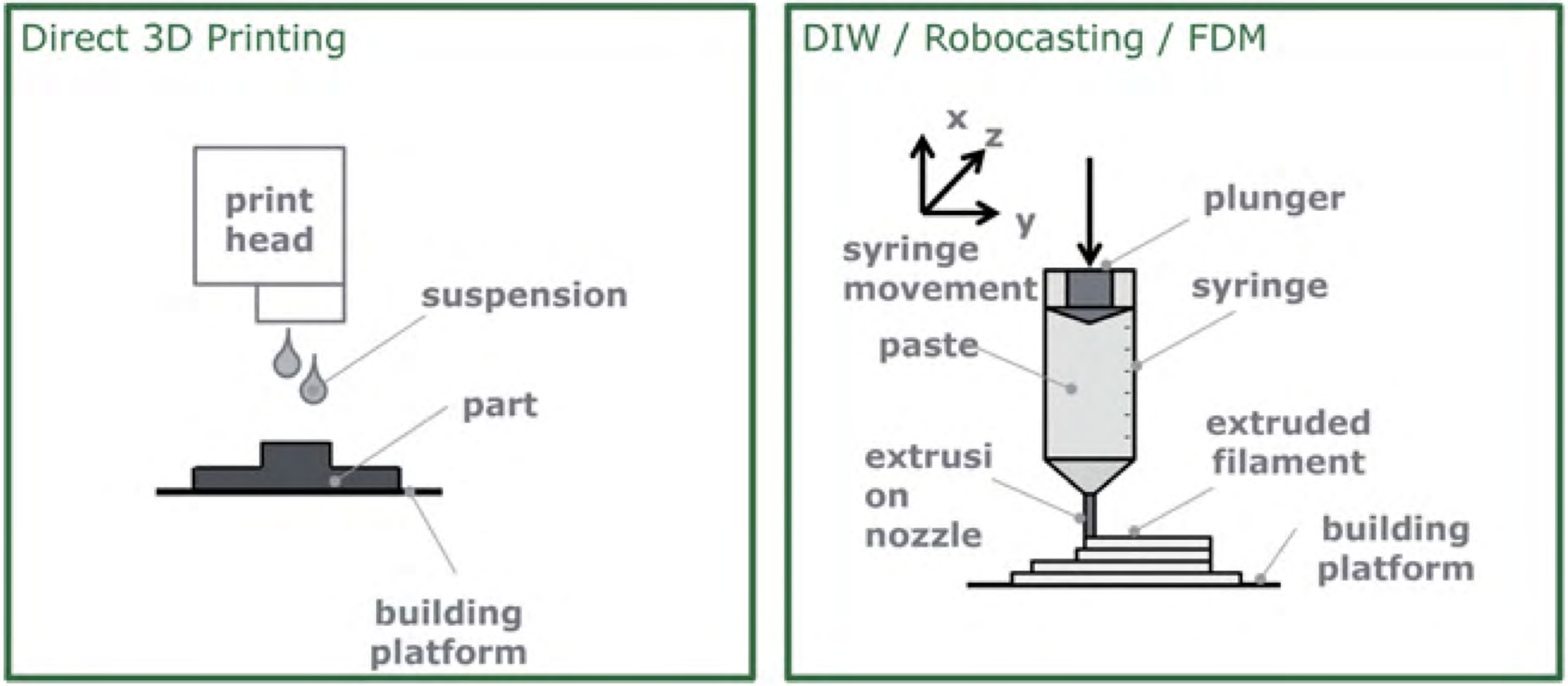
- Additive manufacturing of ceramics and glasses
- Highly porous ceramic structures and foams
- Polymer derived ceramics and geopolymers
- Biosilicates

Indirect 3D printing for ceramics



A. Zocca, P. Colombo, C.M. Gomes, J. Guenster., “Additive Manufacturing of Ceramic-Based Materials,” J. Am. Ceram. Soc., 98 (2015) 1983–2001

Direct 3D printing for ceramics



N. Travitzky et al., Additive Manufacturing of Ceramic-Based Materials, Adv. Eng. Mater., 16 (2014) 729–754

Direct and indirect AM - pros and cons

Direct AM

PROS
- better adhesion between layers
- rheology optimisation
- higher densities
- higher spatial flexibility

CONS
- limited by reaction times
- limited complexity without support material
- heat development can cause issues

Indirect AM

PROS
- higher speeds
- simpler rheology requirements
- higher material and design flexibility
- filler can adsorb heat

CONS
- poorer adhesion between layers
- higher residual porosity
- lower spatial flexibility
- complex powder mixture required to assure flowability:

$$H = \frac{\rho_{\text{Tapped}}}{\rho_{\text{Bulk}}}$$

Why geopolymers?

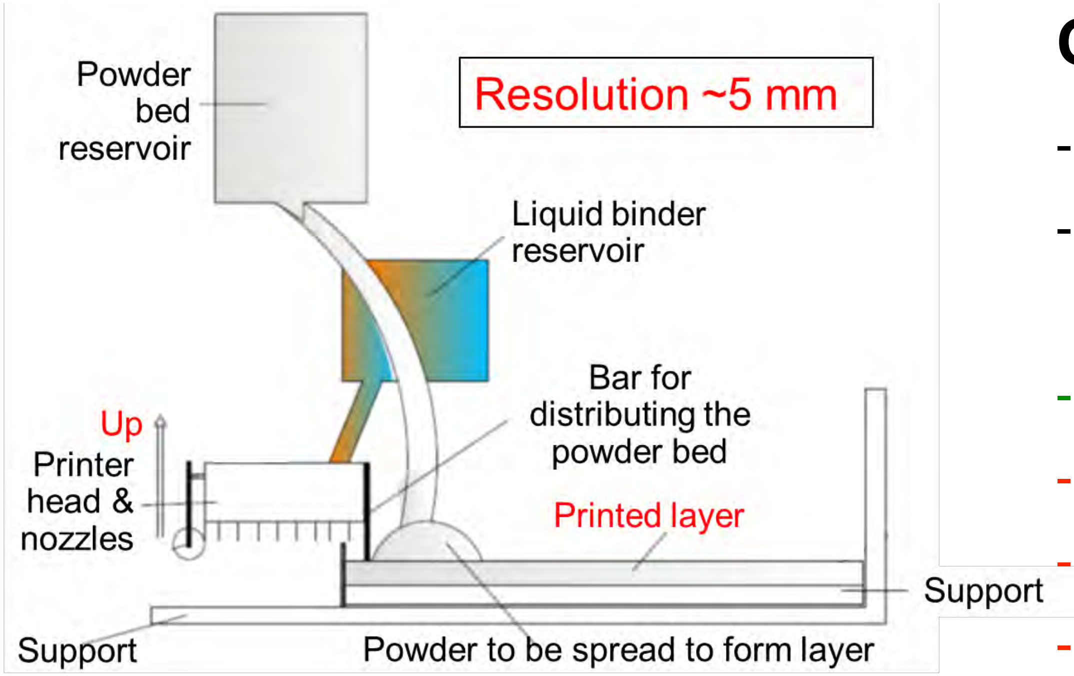
FEATURES:

- Cheap and sustainable raw materials (wastes)
- room T consolidation
- fast setting reactions
- low CO_2 emissions during production
- dense gel-like structure with intrinsic pseudo-plasticity

CHALLENGE: 4D PRINTING

DESAMANERA

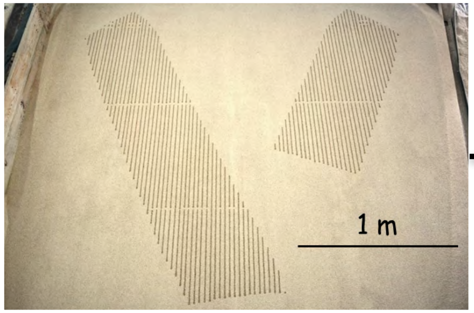
Printing mechanism



Original binder

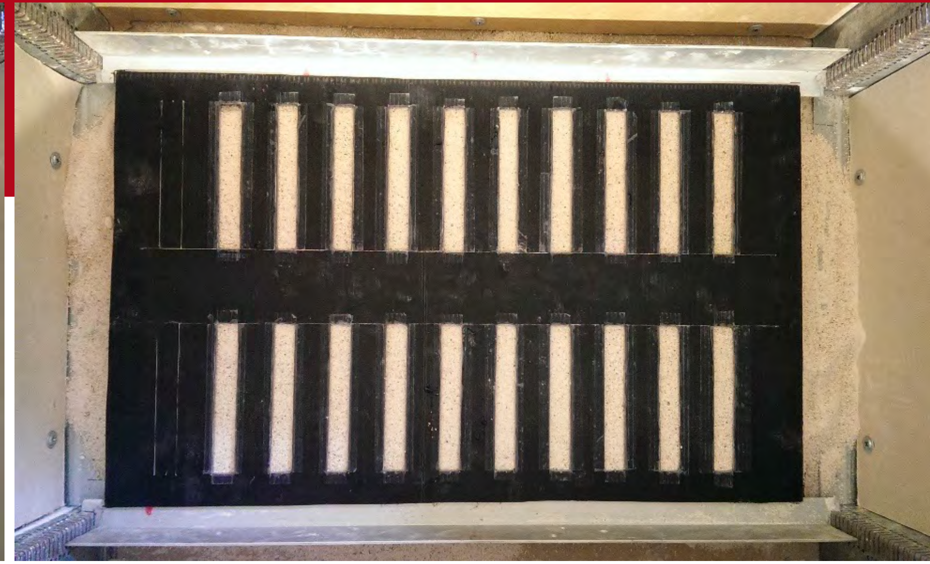
- Magnesium oxide in the powder bed
- Clorurate solution as liquid binder

- adequate mechanical properties
- high residual porosity
- slow setting
- non-hydraulic cement



Validation of the lab procedure

- original binder → same density and mechanical properties as printed parts
- constant volume of binder



Samples: 10x1.5x1.5 cm^3

Geopolymer formulation

Na-based MK-750 geopolymer

Water content optimisation

→ influence on reactivity, wettability, rheology

Water content not optimised

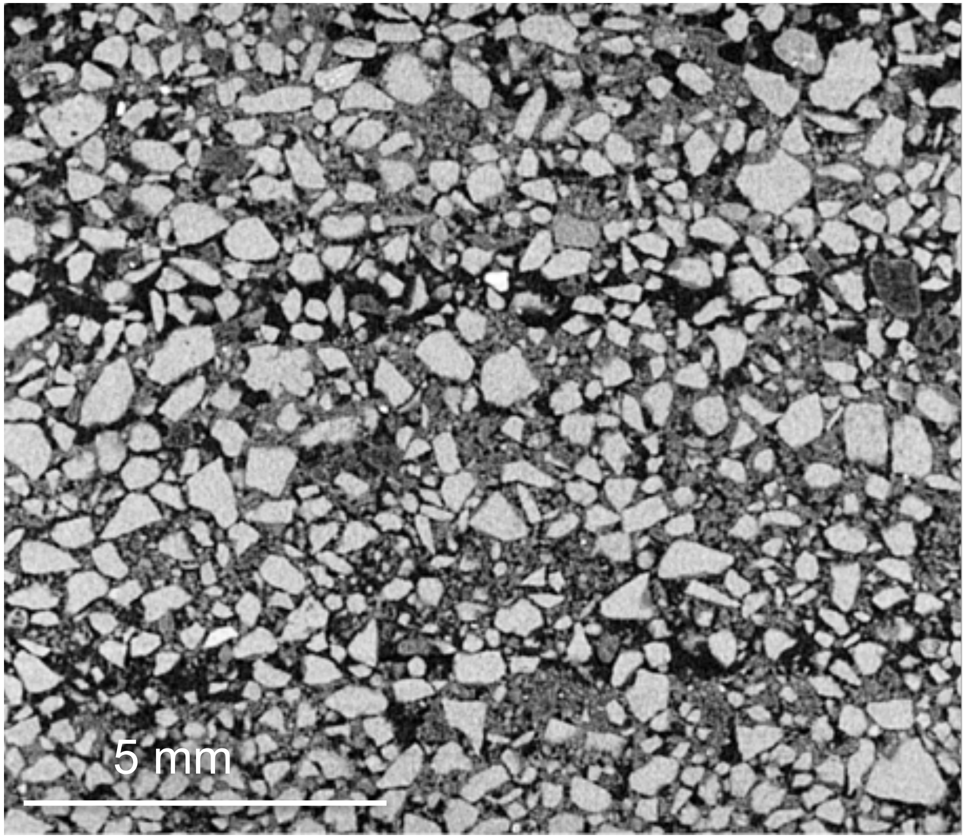
Microstructure

Original binder

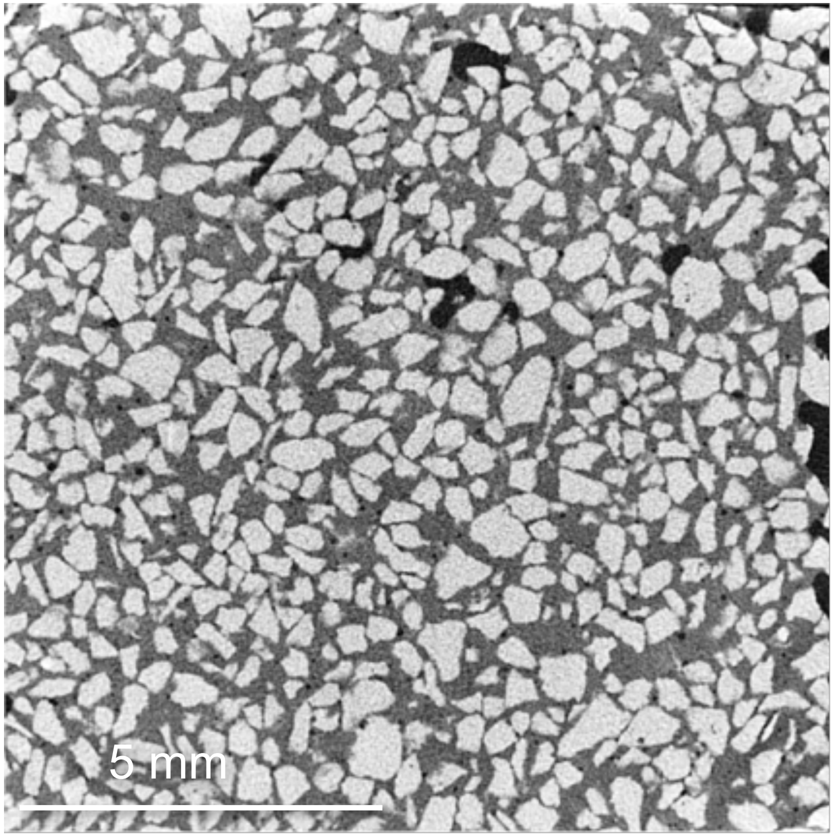
Geopolymer

- Interface between layers still visible
- lower residual porosity

Microstructure

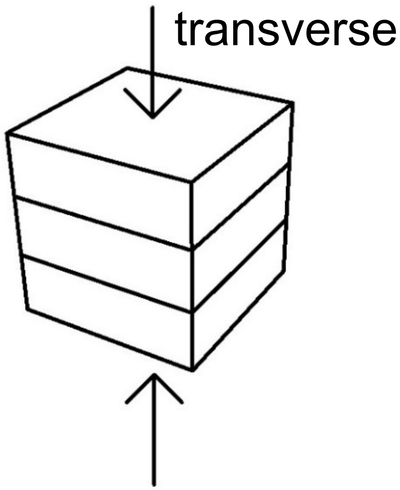


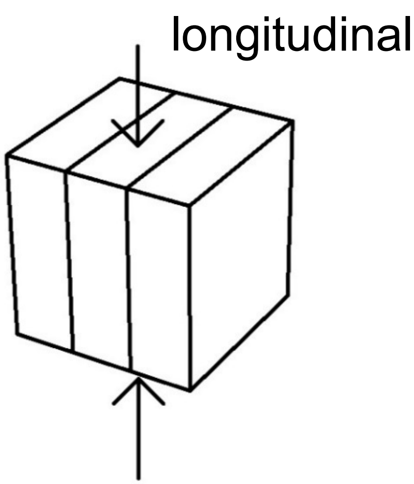
Original binder



Geopolymer

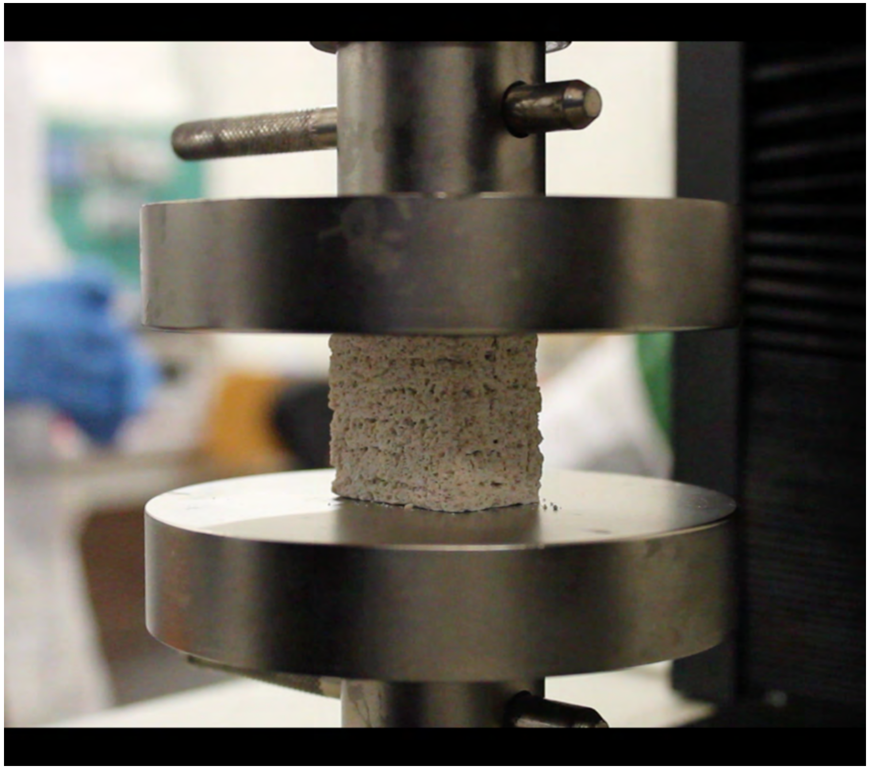
Mechanical properties





Interface between layers

→ **anisotropic behaviour**



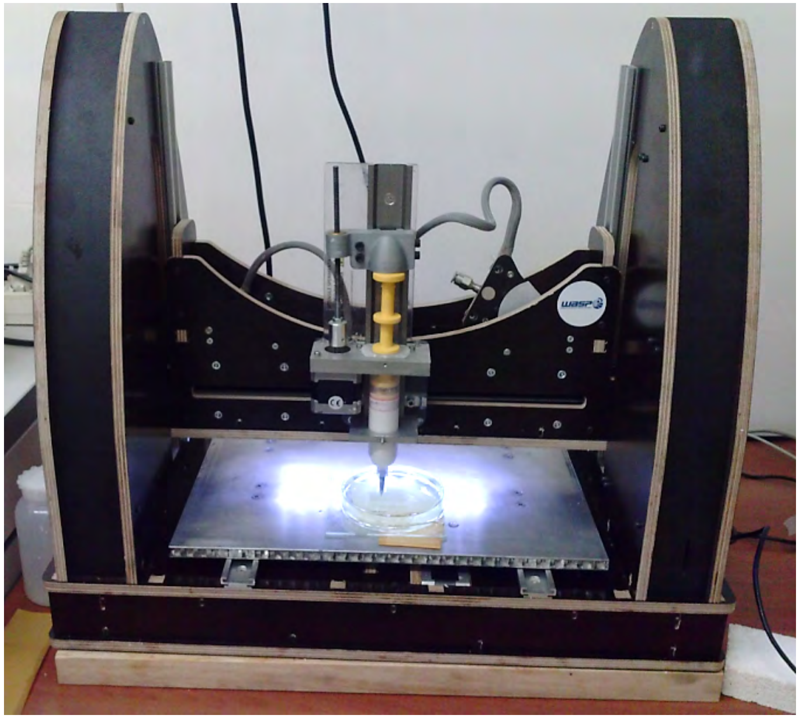
Mechanical properties and density

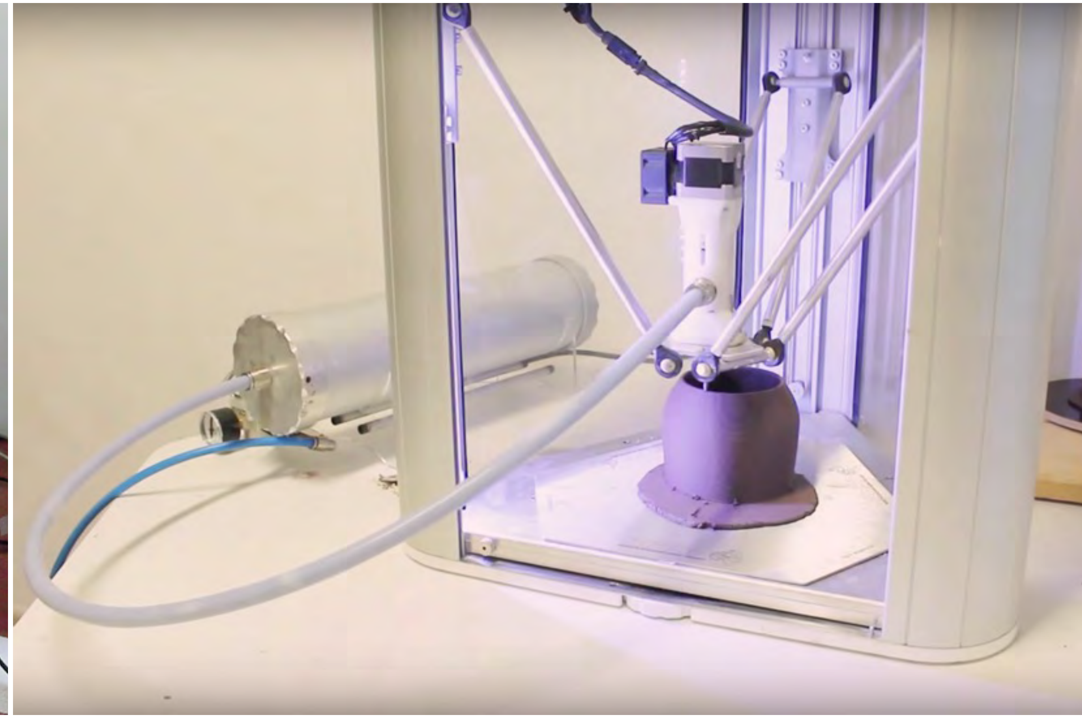
Binder	σ_{COMPR} transverse (MPa)	$\frac{\sigma_{Geo}}{\sigma_{Original}}$	σ_{COMPR} longitudinal (MPa)	$\frac{\sigma_{Geo}}{\sigma_{Original}}$	Mean open porosity (vol%)
Original	1.58 ± 0.11	415%	2.13 ± 0.05	772%	43.8 ± 2.1
Geopolymer	6.56 ± 2.16		16.45 ± 3.50		30.4 ± 2.5

- **Significant increase of mechanical properties and durability**
- **Significant decrease of residual porosity**

- Need of adapting the printer for the new binder

Direct AM of geopolymers





Nozzle size: 100 to 1500 μm

X & Y axis resolution: 120 μm

Z axis resolution: 4 μm

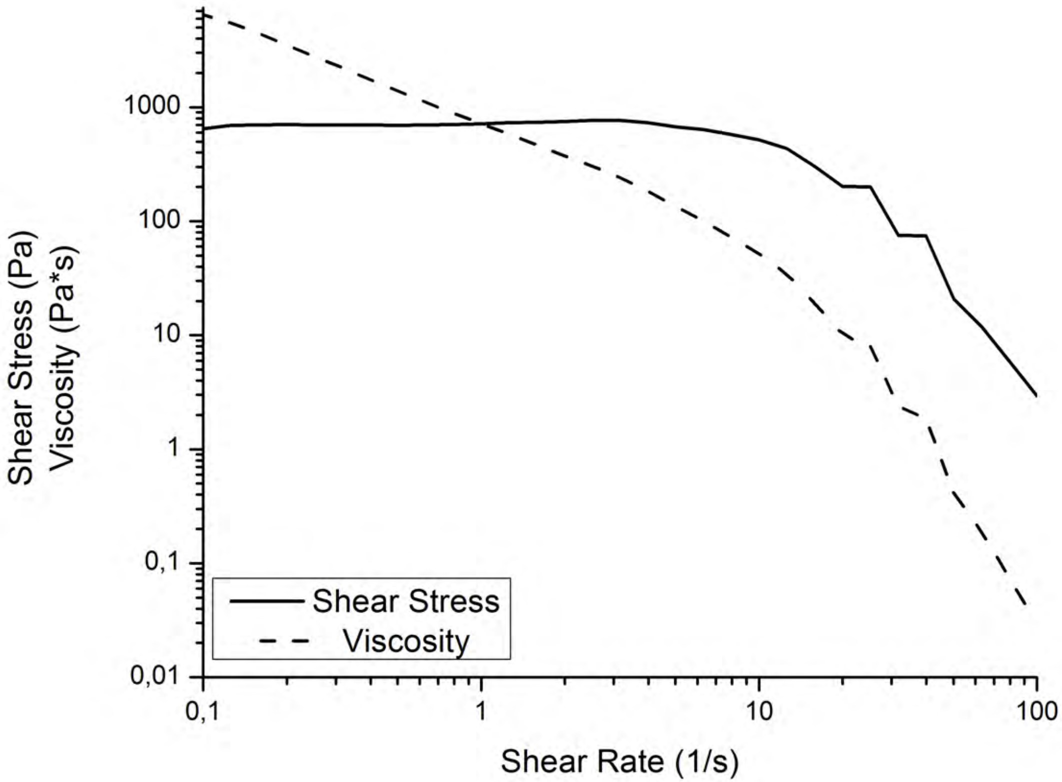
CHALLENGE

thin walls and spanning features

→ optimisation of the ink rheology

→ use of additives

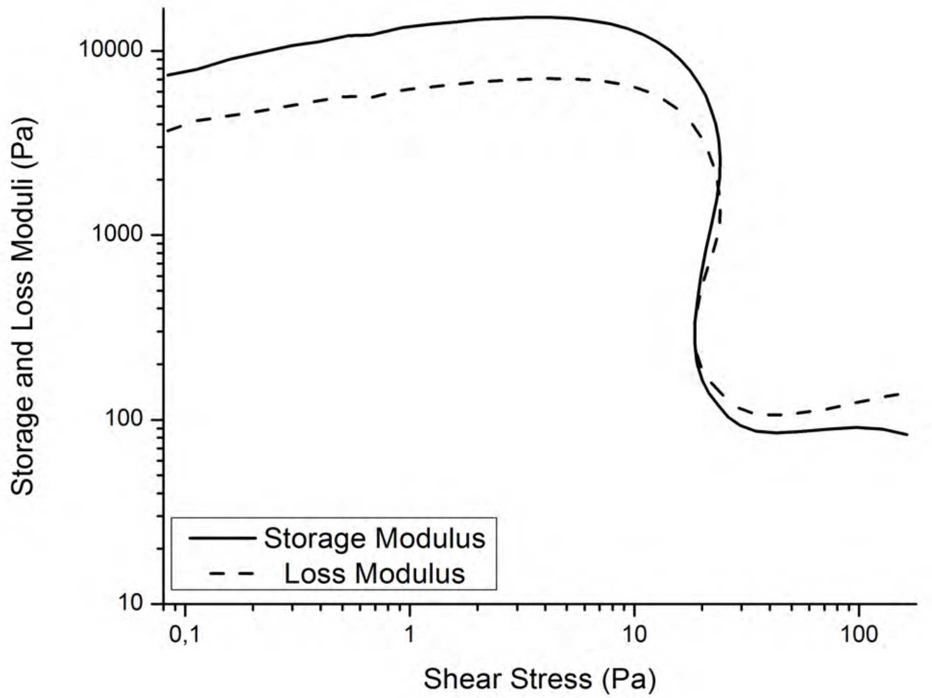
Ink features



flow curve, shear rates ramping from 0.1 1/s to 100 1/s

- Formation of 3D poly(sialate-siloxo) network → viscosity increase with time
- Intrinsic **pseudo-plastic behaviour** + <u>additives</u>
- Limited working time

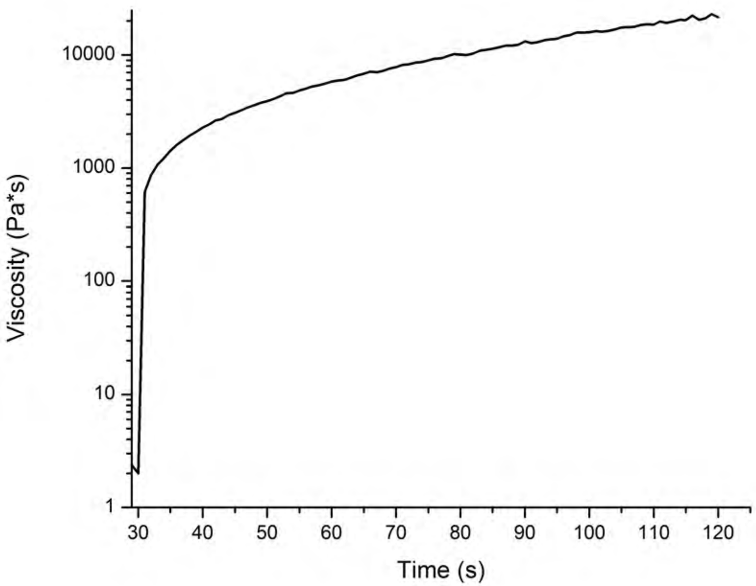
Ink features



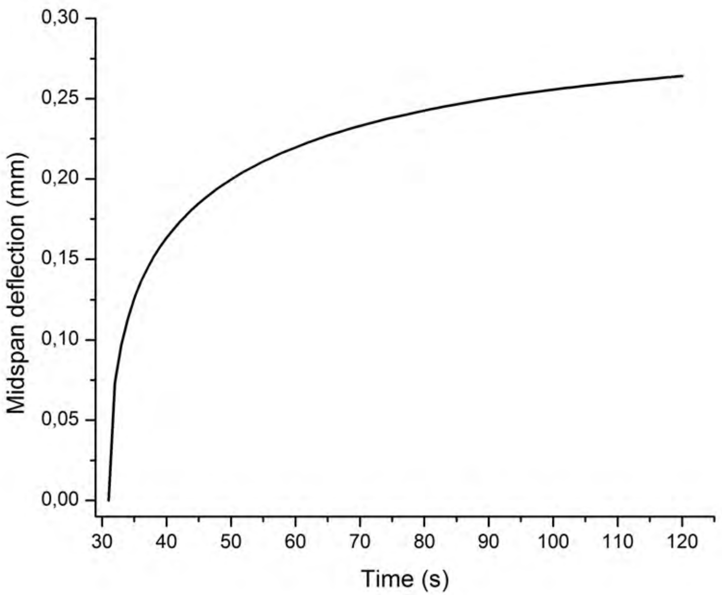
strain sweep test, strain ramping logarithmically from 0.001% to 100% at 1Hz frequency

- physical, reversible **gel** formation
- initial **yield stress** → prevents spontaneous flow

Ink features



viscosity recovery test



midspan deflection evaluation

Fast increase in viscosity after extrusion

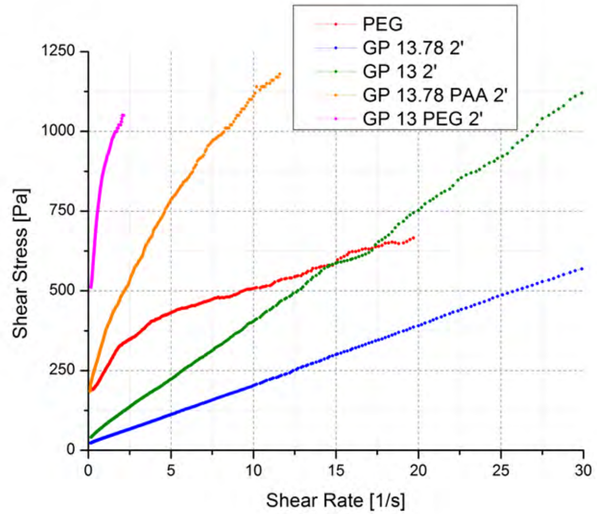
→ **low deflection** for printed overhang structures or spanning features

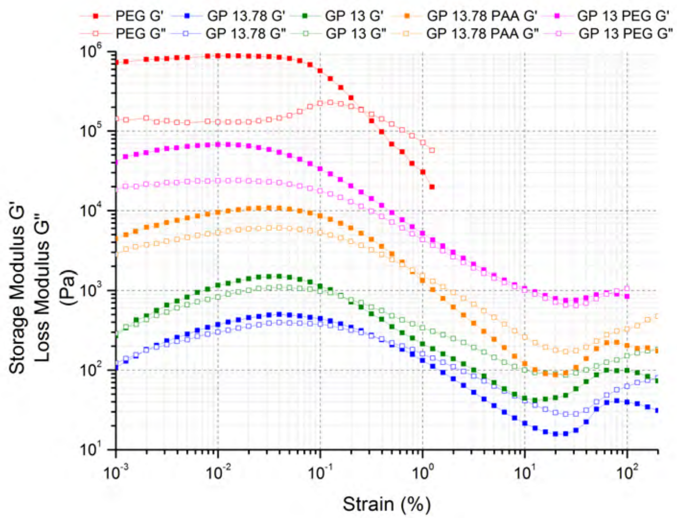
Spanning distance: 2 mm

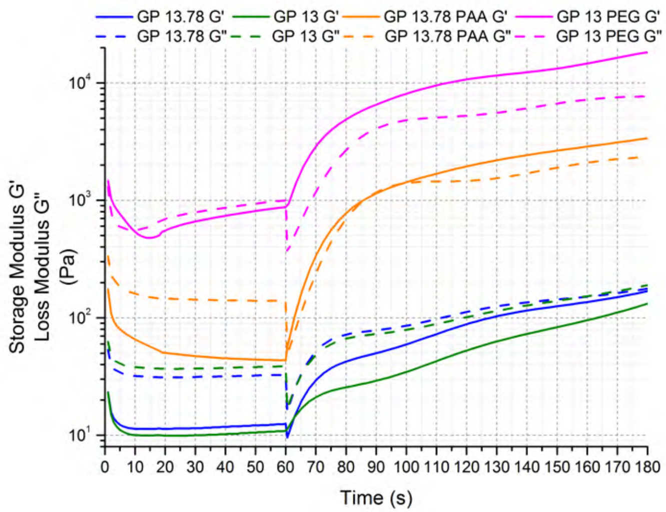
Filament diameter: 0.84 mm

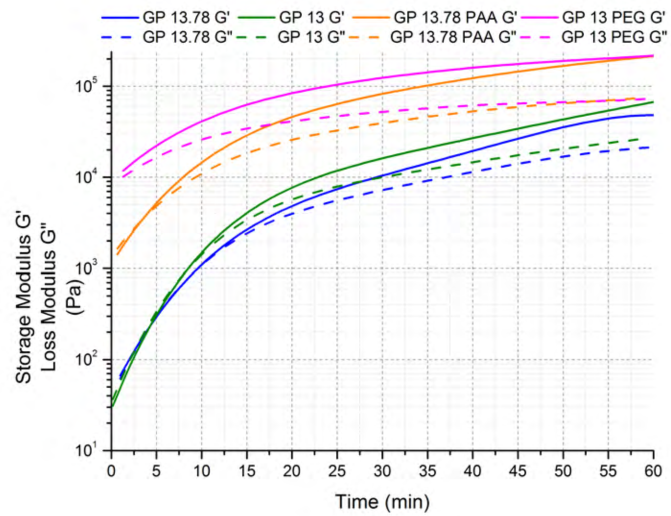
Deflection **~0.25 mm**

Ink development and optimisation

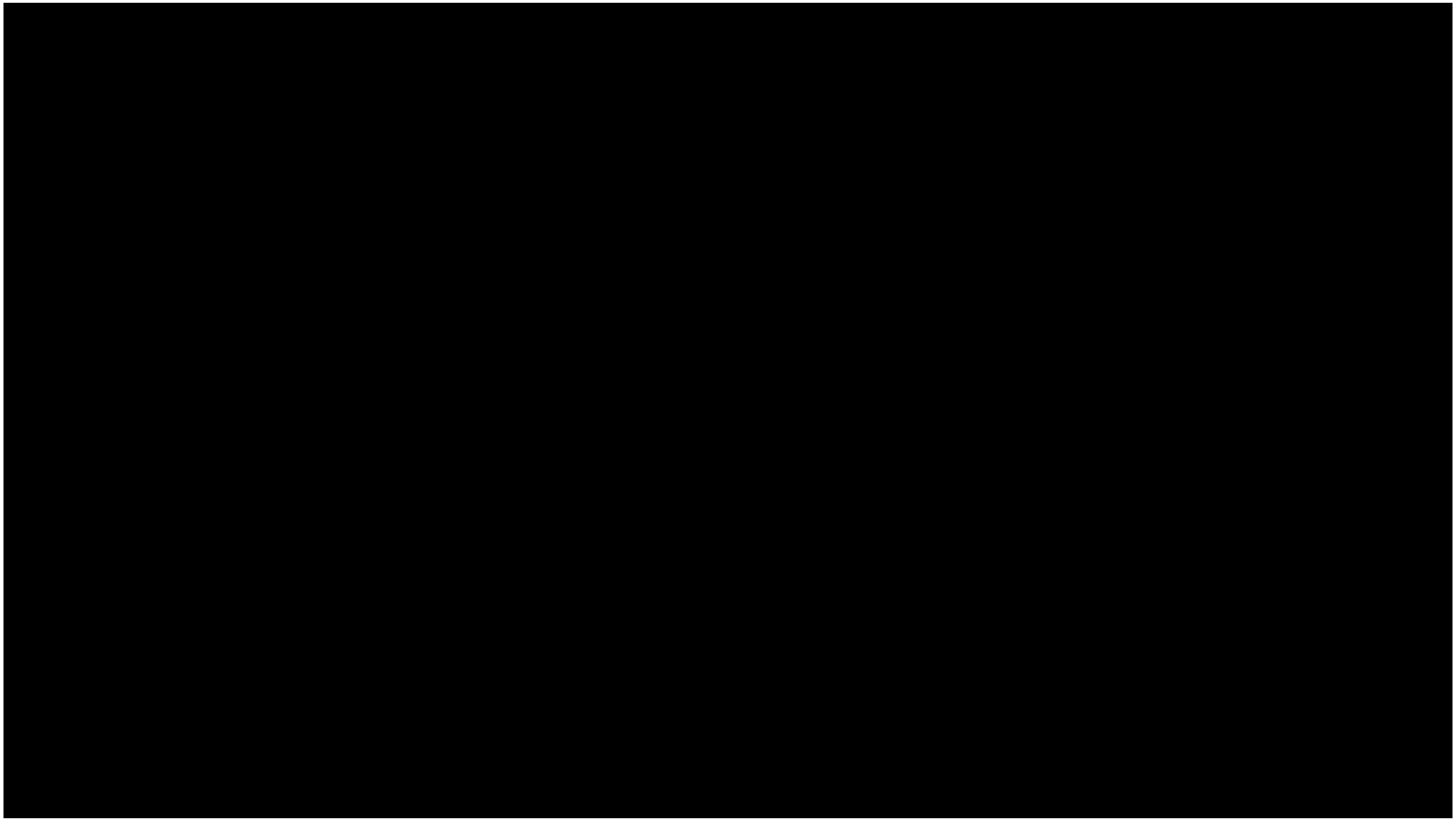


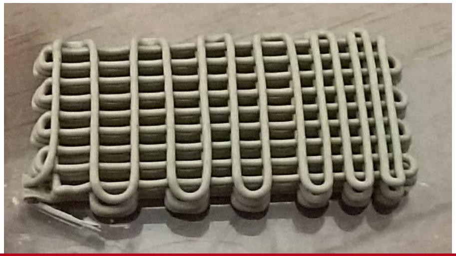




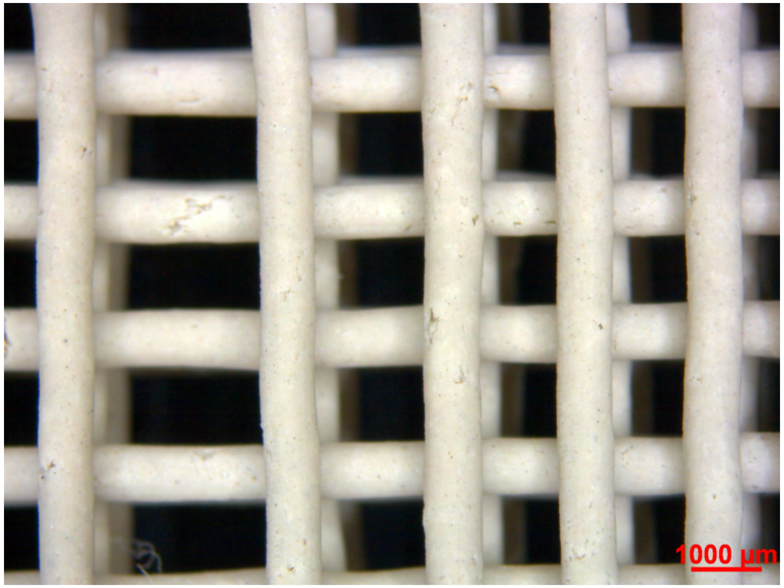


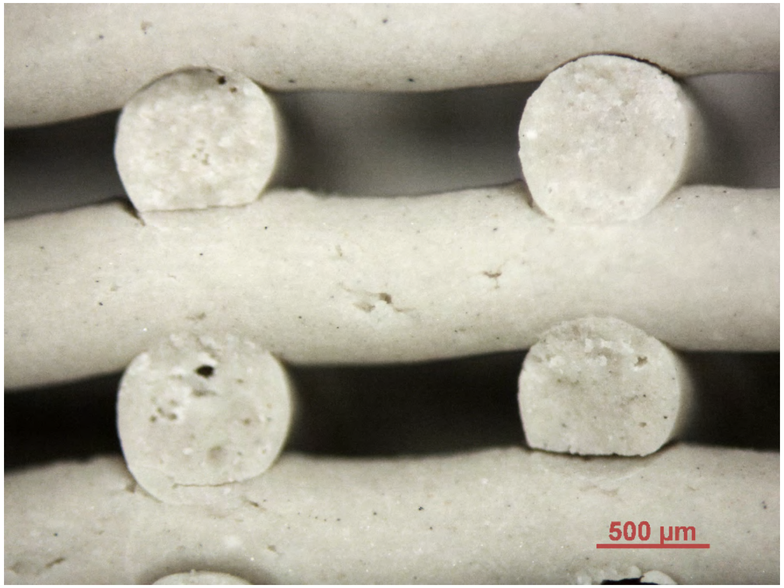
Process overview





Mix optimisation





Regular structure

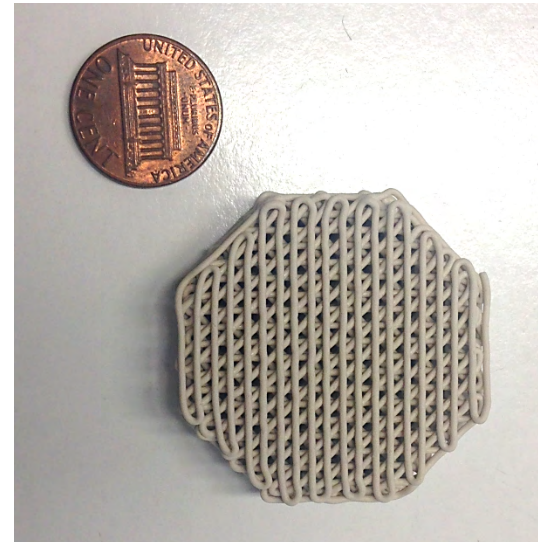
No sagging of filaments

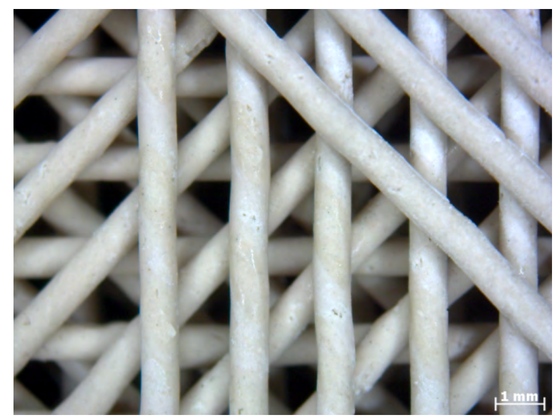
→ increasing spanning lengths

Good interface between filaments

Results

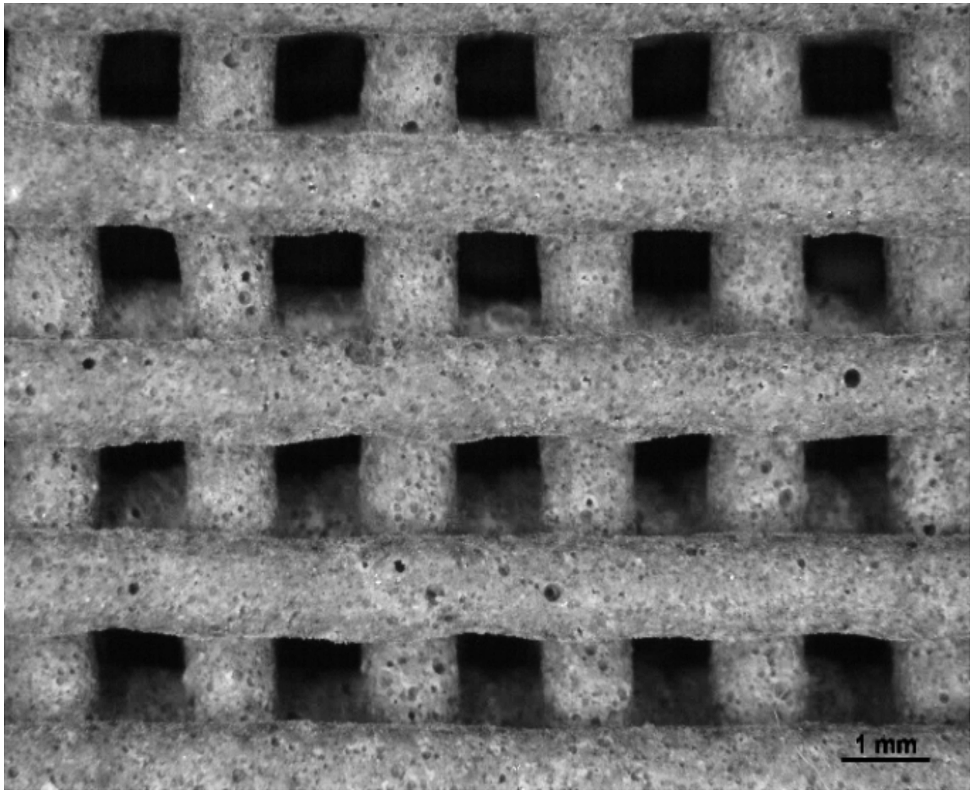
Increased complexity





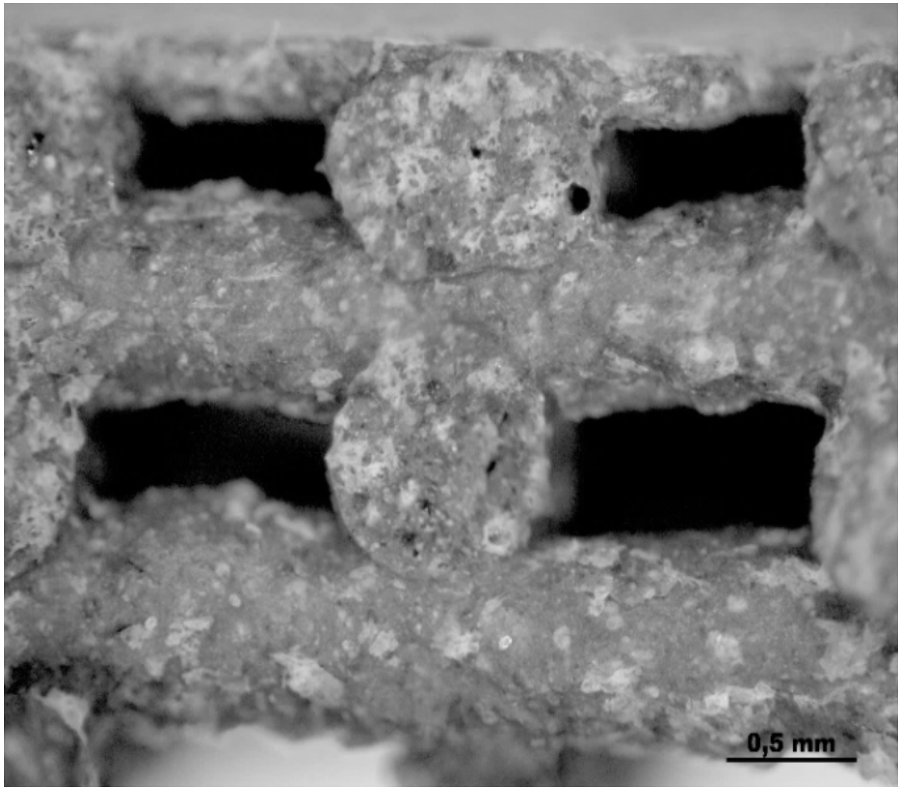
Proposed application:
filters

Experimentation on different inks



Fly ashes addition

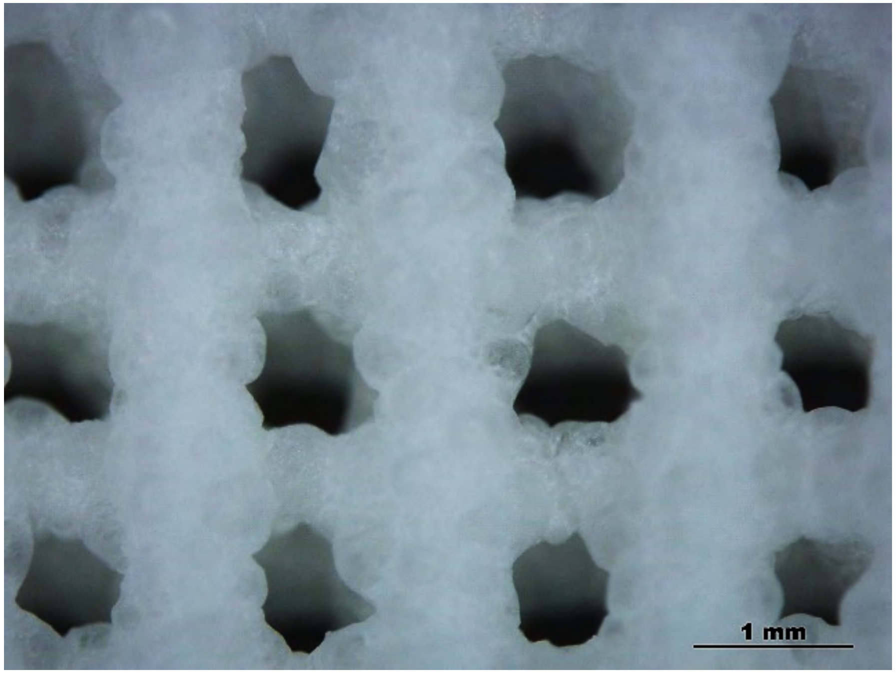
+ pseudo-plasticiser, retarding agent



K-based geopolymer

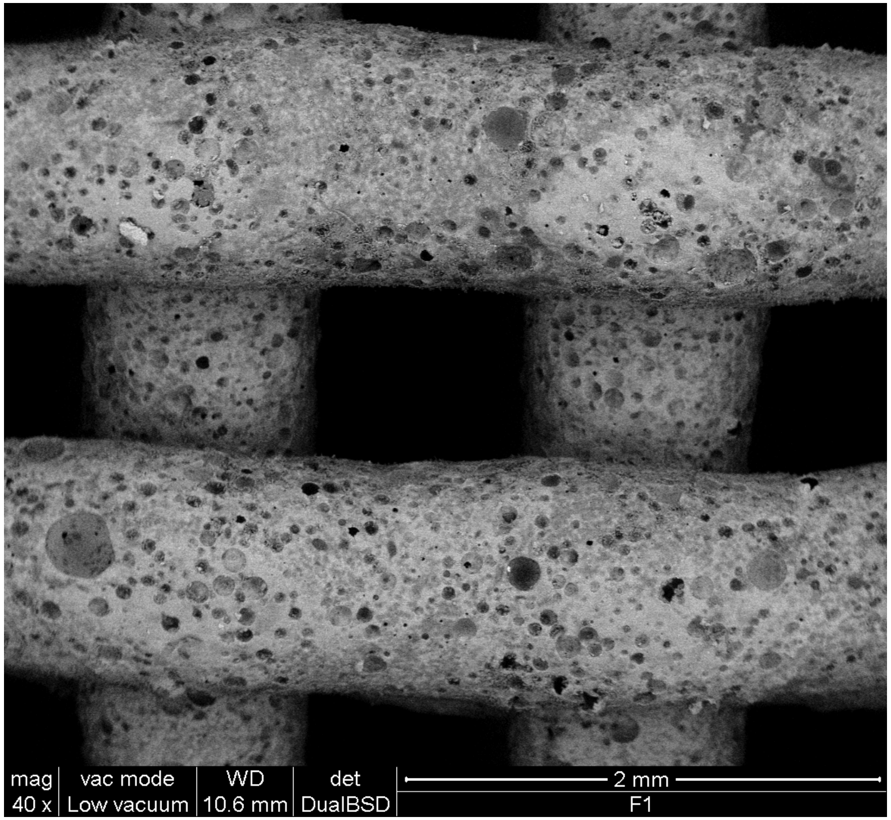
leucite formation after heat treatment

Experimentation on different inks



Porous struts

Hierarchical porosity



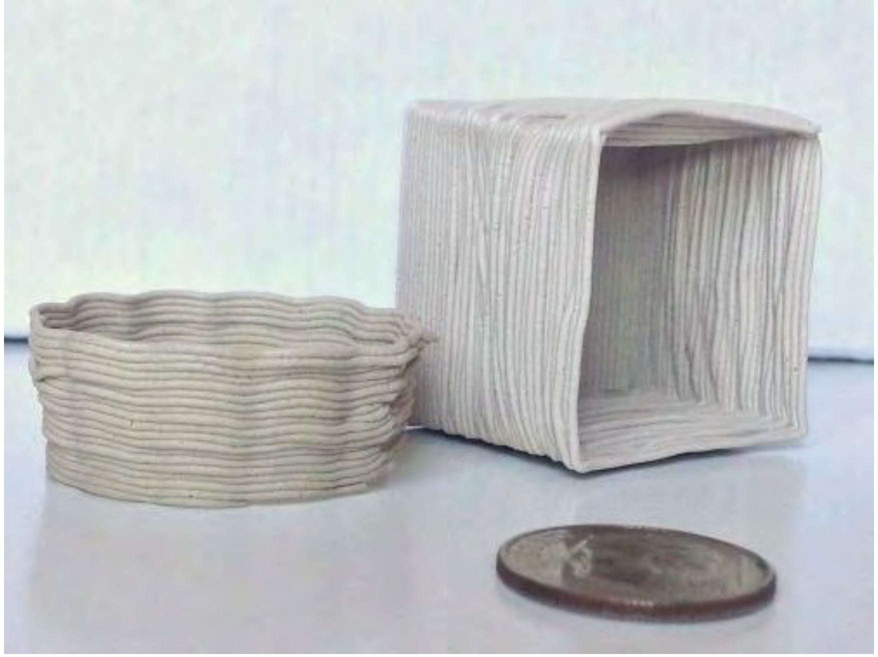
Na-based geopolymer

nepheline formation after heat treatment

Conclusions

- Geopolymers have been used as binders for indirect AM

- Geopolymer inks have been printed via DIW



FUTURE GOALS:
- increase repeatability
- widen materials window

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Thank you
for your attention!