CNC as a biodegradable aid to improve 3D printing of cementitious materials

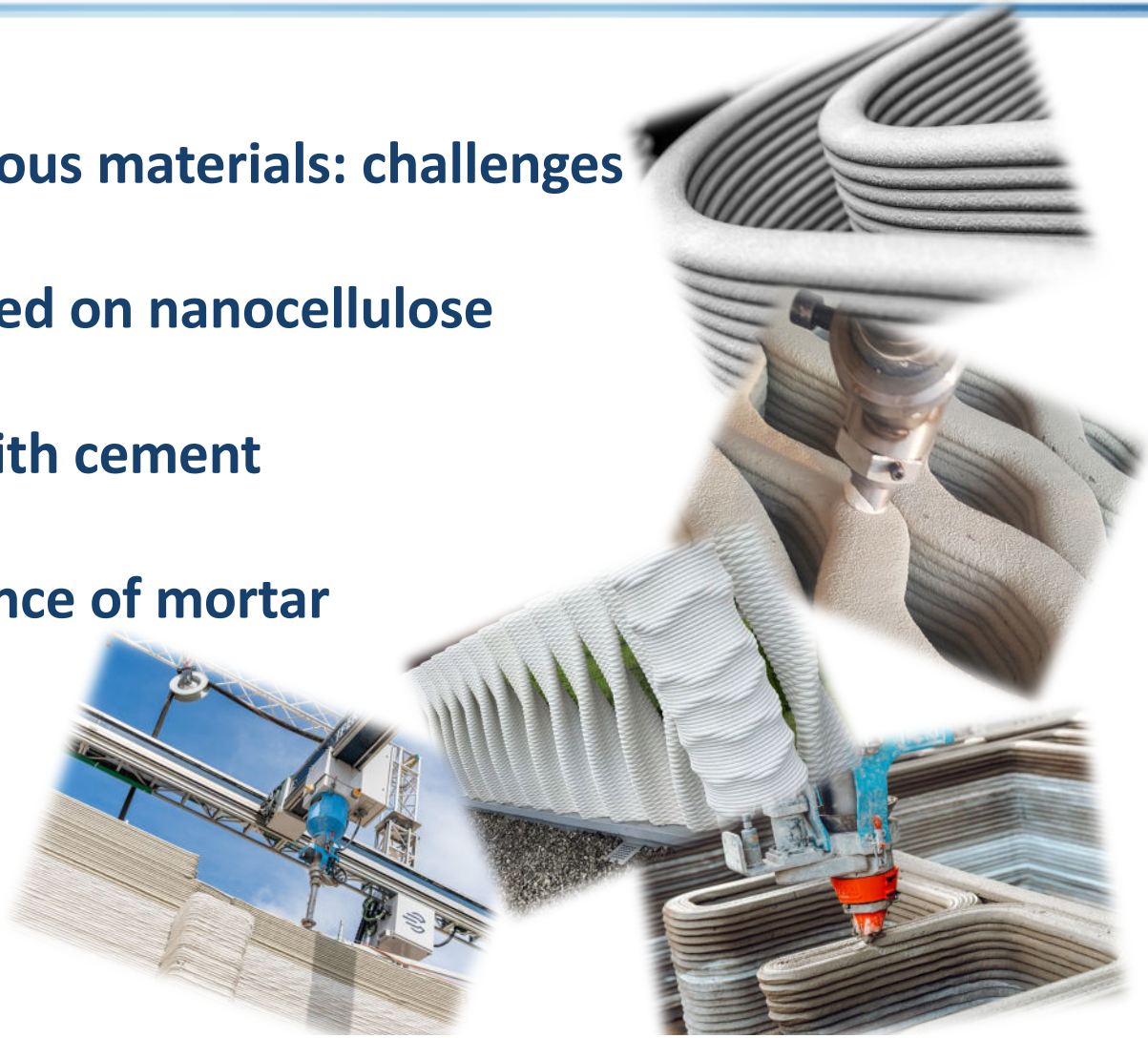
C Negro, R. Jarabo, E. Fuente, P. Carballosa, JL García and **A. Blanco**

ablanco@ucm.es

Complutense University of Madrid
Cellulose, Paper and Advanced Water Treatments
Chemical Engineering Department

Contents

- 3D printing of cementitious materials: challenges
- A potential solution based on nanocellulose
- Interactions of NC/SP with cement
- Effects on the performance of mortar
- Conclusions



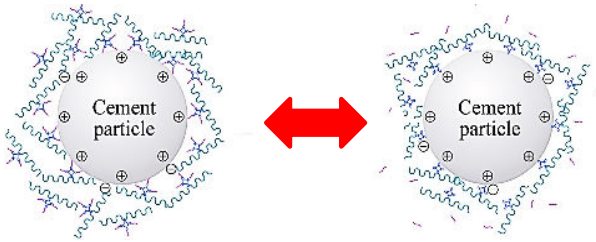
3D printing challenges

Homogeneous mix

Non-stop process

Easy flow through the nozzle
High workability

- Dispersibility
- Fluidity
- Slow hydration



Non biodegradable
Difficult control:

- % RM
- T
- Morphology
- Shearing forces

Self-supporting layers

Fast development of compressive strength

- Aggregation
- Low fluidity
- Fast hydration

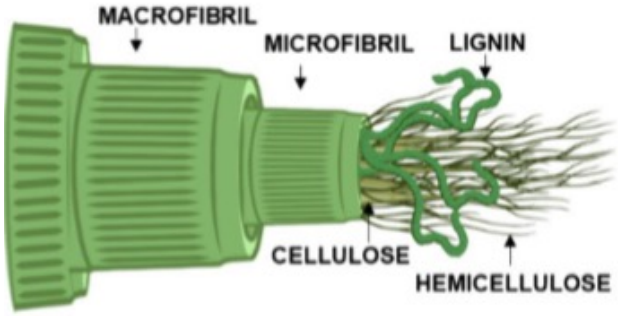
SUPERPLASTIZISERS

Improve fluidity
Reduce w/c ratio
Control hydration rate
Increase strength

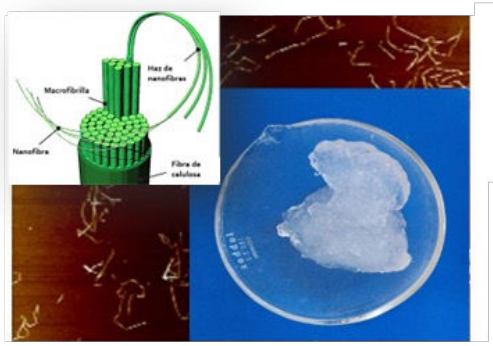
- sulfonated melamine formaldehyde
- sulfonated naphthalene formaldehyde
- modified lignosulphonate
- polycarboxylate ethers
- polystyrene sulphonates
- polyacrylates, etc.

3D printing improvement with NC

Could NC contribute to solve these challenges?



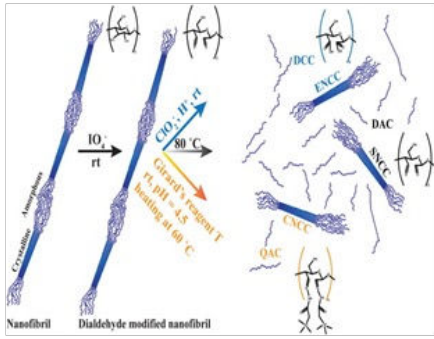
Nanofibrillated cellulose



D:2-50 nm, L: 0,2-2 µm
L/D > 200

Nanocryistaline cellulose

Hairy Cellulose



CNC with functionalized polymeric chains
Oxidation + heating

IIBCC 2024 COLOMBO | SRI LANKA

Production of CNC

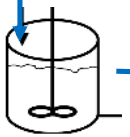
Cotton

Grinding

H_2SO_4 60%
14 L/kg

Acid hydrólysis
45min 45ºC

H_2O



Dilution
1-10

4500g (RCF)
10min

Dialysis
until pH =7

Sonication until
turbidity <100 NTU

CNC suspension

Lyophilization
-80ºC 0,001 bar

CNC powder

Cement

Type I Portland (CEM I 52.5R)

Superplastiziser

(Poly-aryl phosphonic ether) polymer

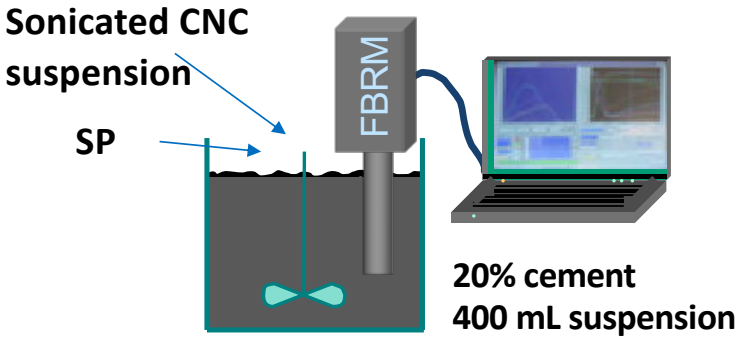
Sand

Siliceous sand (0-2 mm) EN 196-1

CNC characteristics

Yield (%)	61.1±6.0
DAC (%)	32.6±2.5
PD	224.2±4.1
Zeta Potential (mV)	-27±4
CrI (%)	94.4±0.5
Mean length (nm)	148±96
Mean width (nm)	24±8

Interaction of CNC with cement



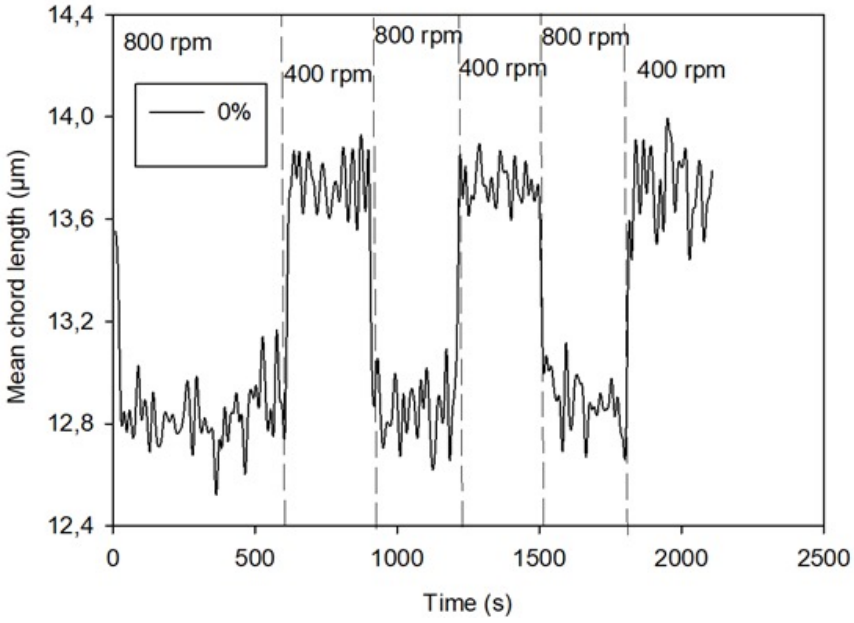
- **Dispersion of cement in water**

  800 rpm 10 min – 400 rpm 5 min - 800 rpm 5 min

- **Addition of CNC or superplastiziser (SP)**

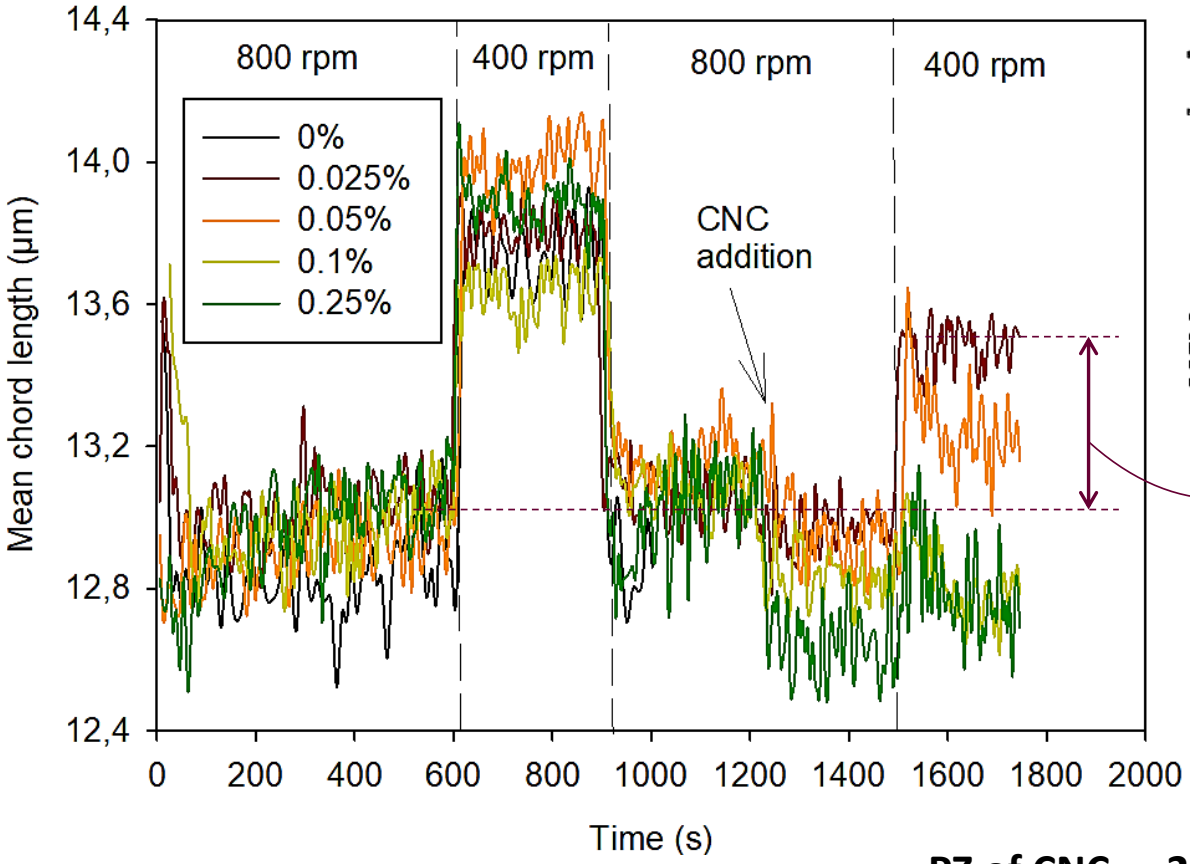
- **Flocculation-deflocculation cycles**

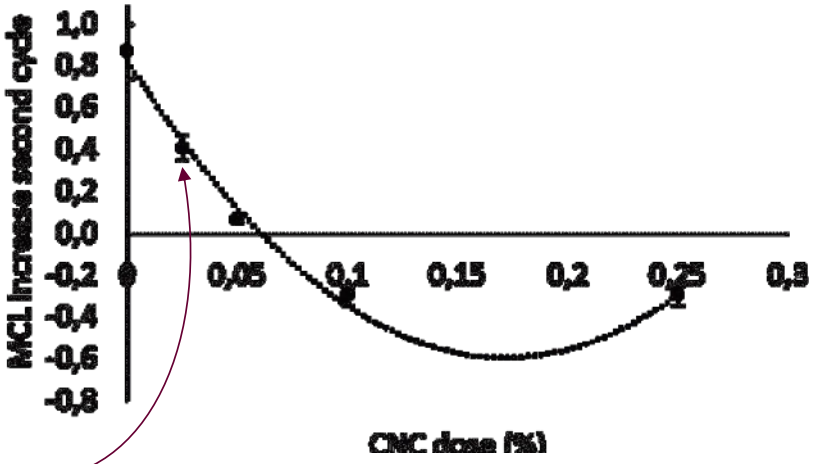
  800 rpm – 400 rpm – 800 rpm - 400 rpm
  5 min 5 min 5 min 5 min



Trial name	SP (%)	CNC (%)	SP (g of commercial product)	CNC (7.2 g/L suspension) (g dry CNC)
REF (0%)	0	0	0	0
0,025%CNC	0	0.025	0	0.02
0,05%CNC	0	0.05	0	0.04
0,10%CNC	0	0.1	0	0.08
0,25%CNC	0	0.25	0	0.2
0.5%SP	0.5	0	0.4	0
0.85% SP	0.85	0	0.68	0
0.25%CNC + 0.5%SP	0.5	0.25	0.4	0.2

Effect of CNC dose on cement dispersion



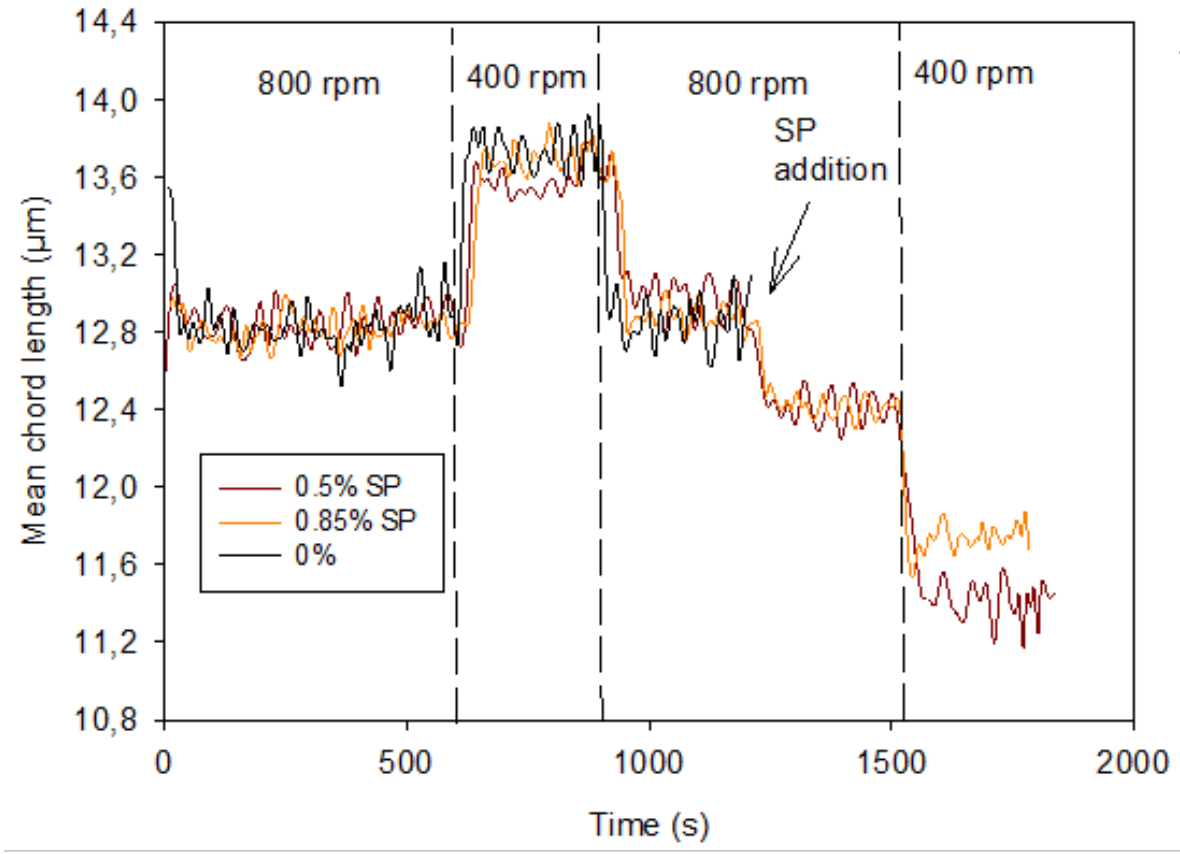


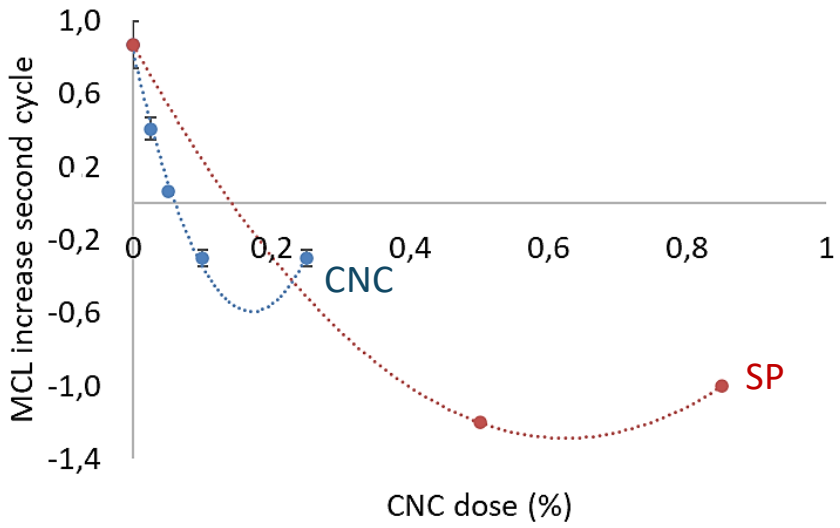
CNC addition

- **increases cement dispersion**
- **avoids cement aggregation when shear forces decreases**

PZ of CNC = -27mV → Electro-steric repulsion

Effect of SP dose on cement dispersion

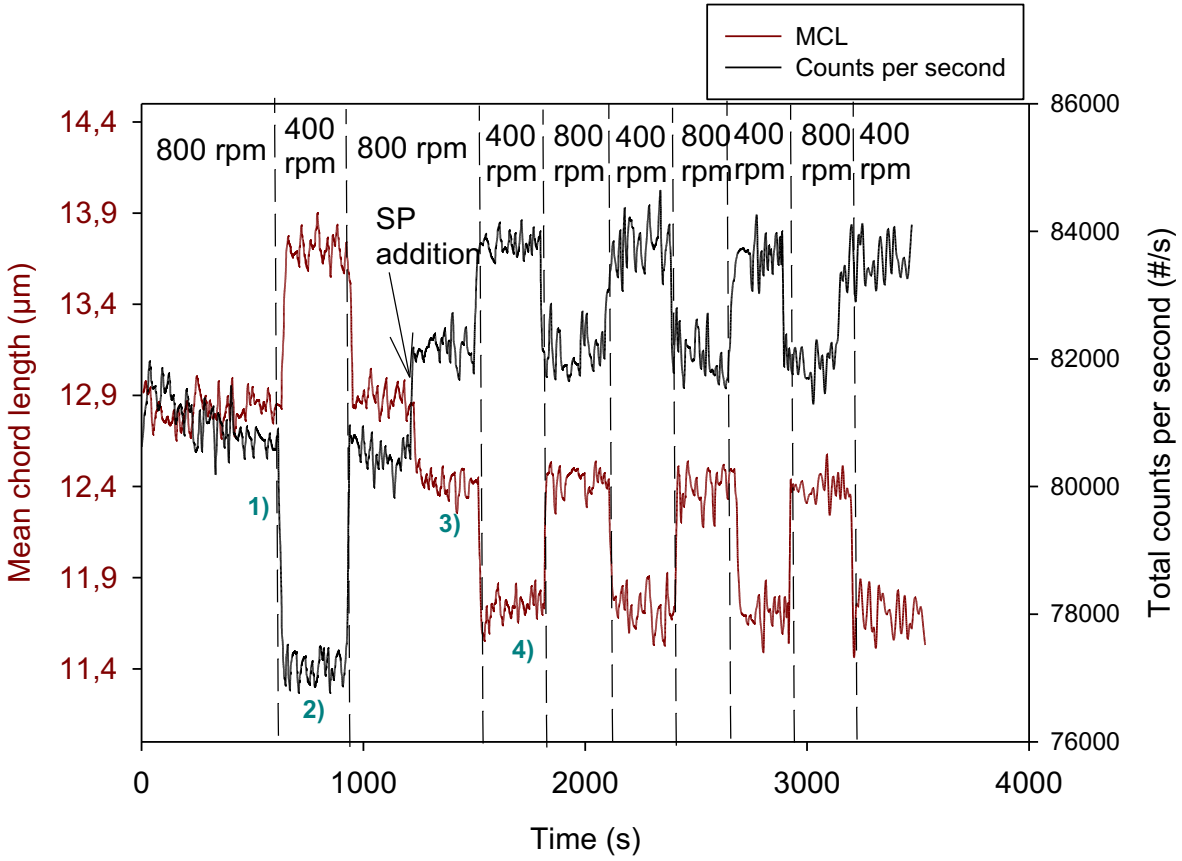




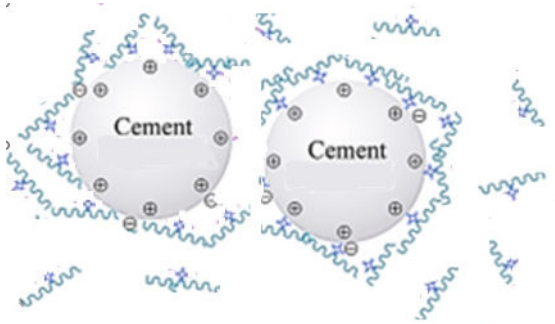
SP addition:

- **increases cement dispersion but requires higher doses than CNC**
- **When shear forces decreases …… dispersion is higher**

Effect of SP dose on cement dispersion

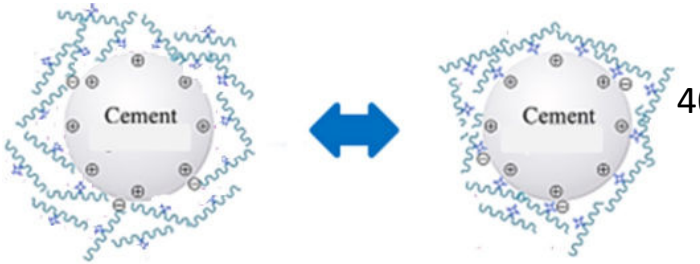


Partial adsorption ➔ partial aggregation



800 rpm

Higher adsorption ➔ stable dispersion

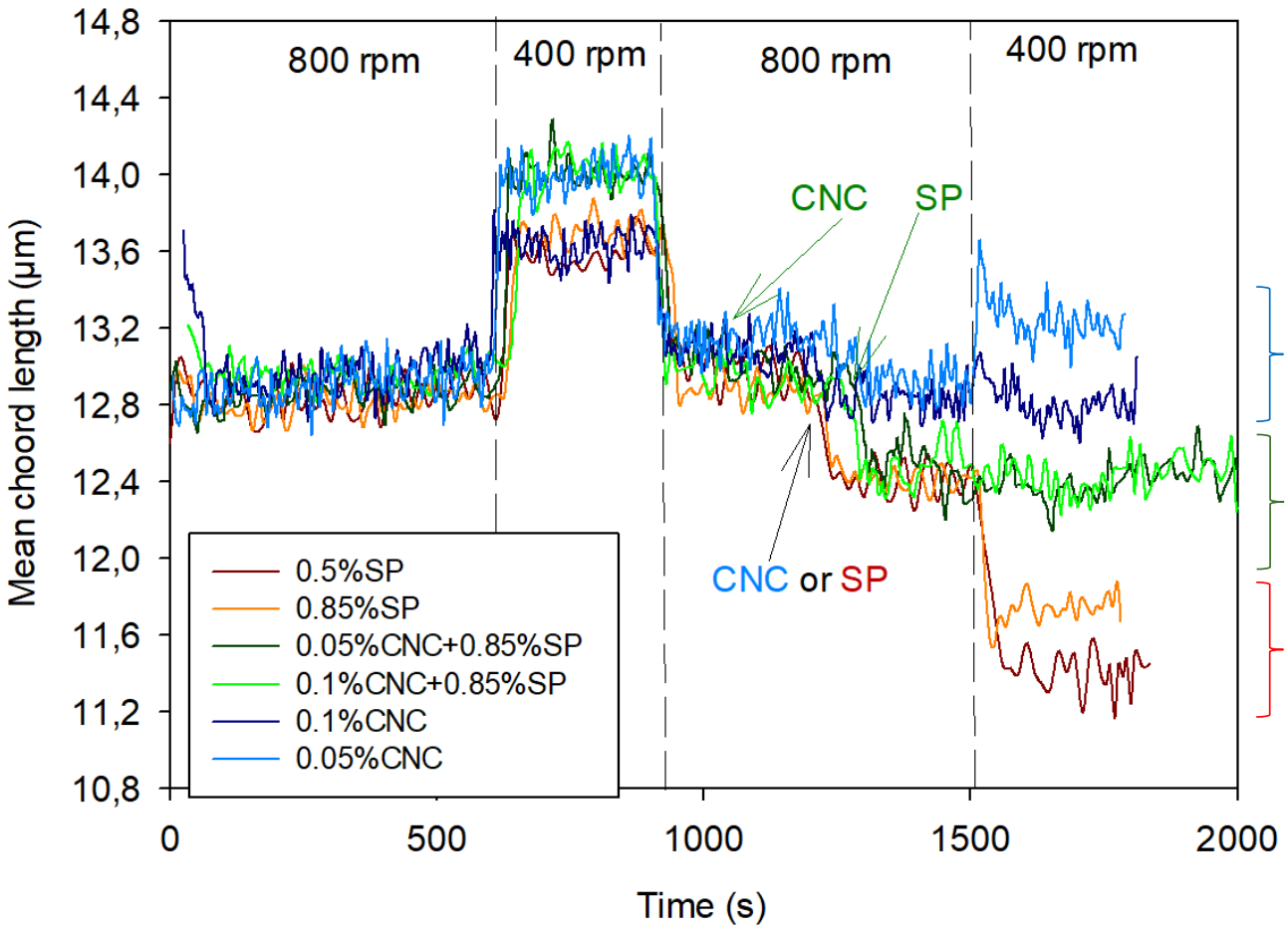


400 rpm

Weak SP adsorption ➔ reversible

Interaction of CNC with SP and cement

Is a synergic effect of CNC and SP on cement dispersión?

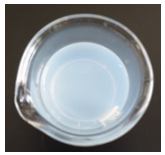


The presence of CNC stabilizes the cement dispersions ➔ easier process control

Effect of CNC on mortar performance

IIBCC 2024 COLOMBO | SRI LANKA

Dispersion of CNC suspension or/and SP in water



Mixture of dry CNC with cement

Water adjusted: flowability > 180 mm

EN 1015-3

Preparation of mortar EN-196-1

EN-196-3

Setting time, hardening

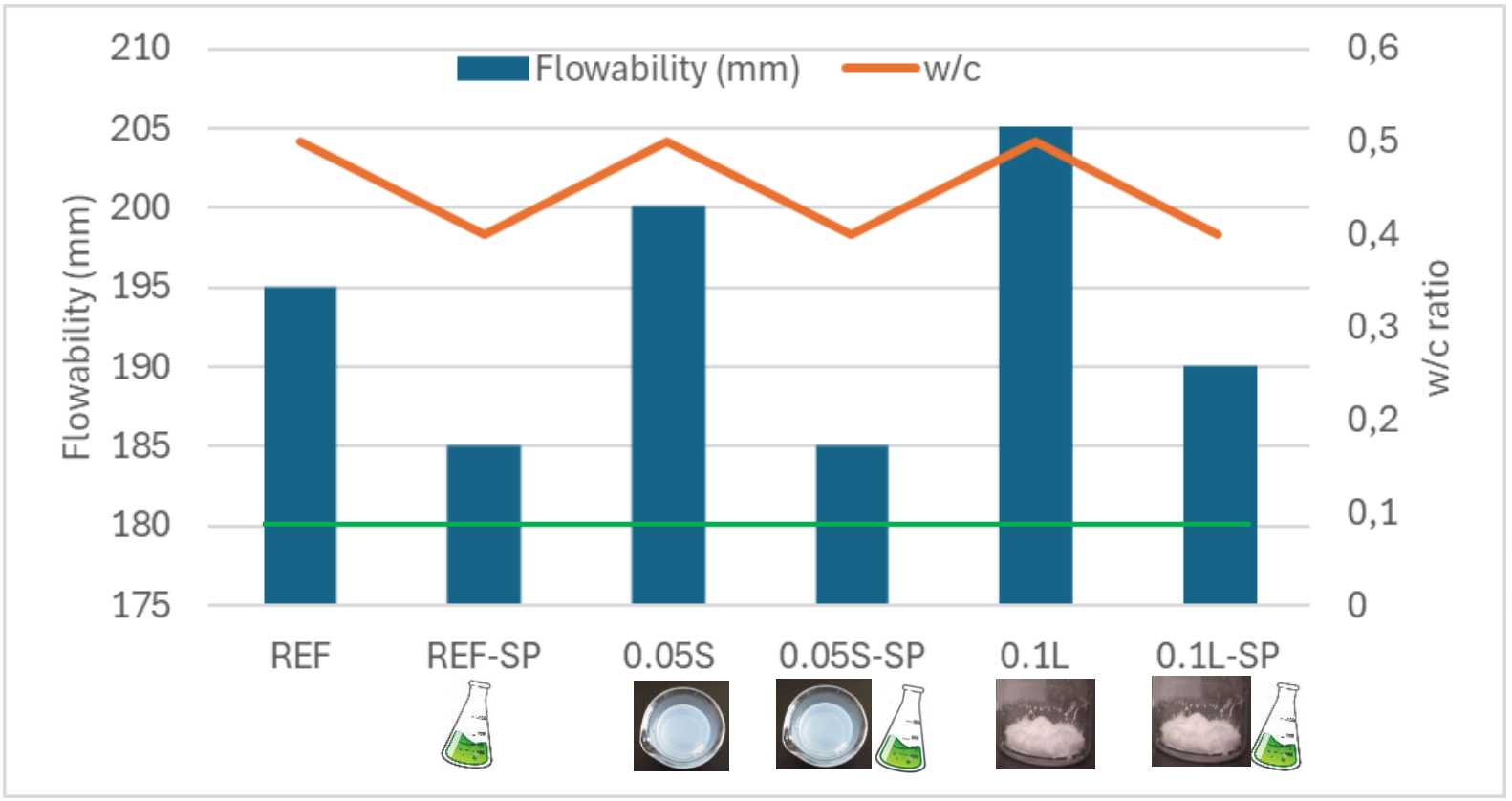
Casting 9 prismatic probes

Compressive Strength

Raw material	REF	REF-SP	0.05S	0.05S-SP	0.1L	0.1L-SP
Cement (g)	450	450	450	450	450	450
Water (g)	225	180	225	180	225	180
Siliceous sand (g)	1350	1350	1350	1350	1350	1350
SP (g)	---	3,8	---	3,8	---	3,8
Suspended CNC (dry g)	---	---	0,41	0,41	---	---
Lyophilized CNC (g)	---	---	---	---	0,82	0,82

Effect of CNC on mortar performance

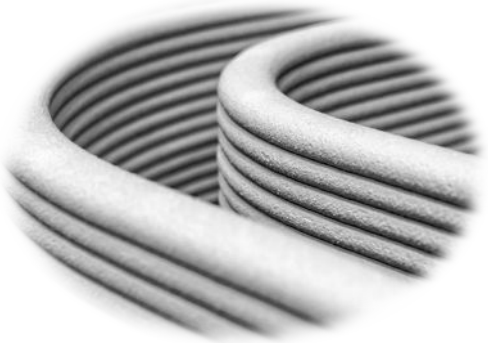
Effect on water demand and flowability

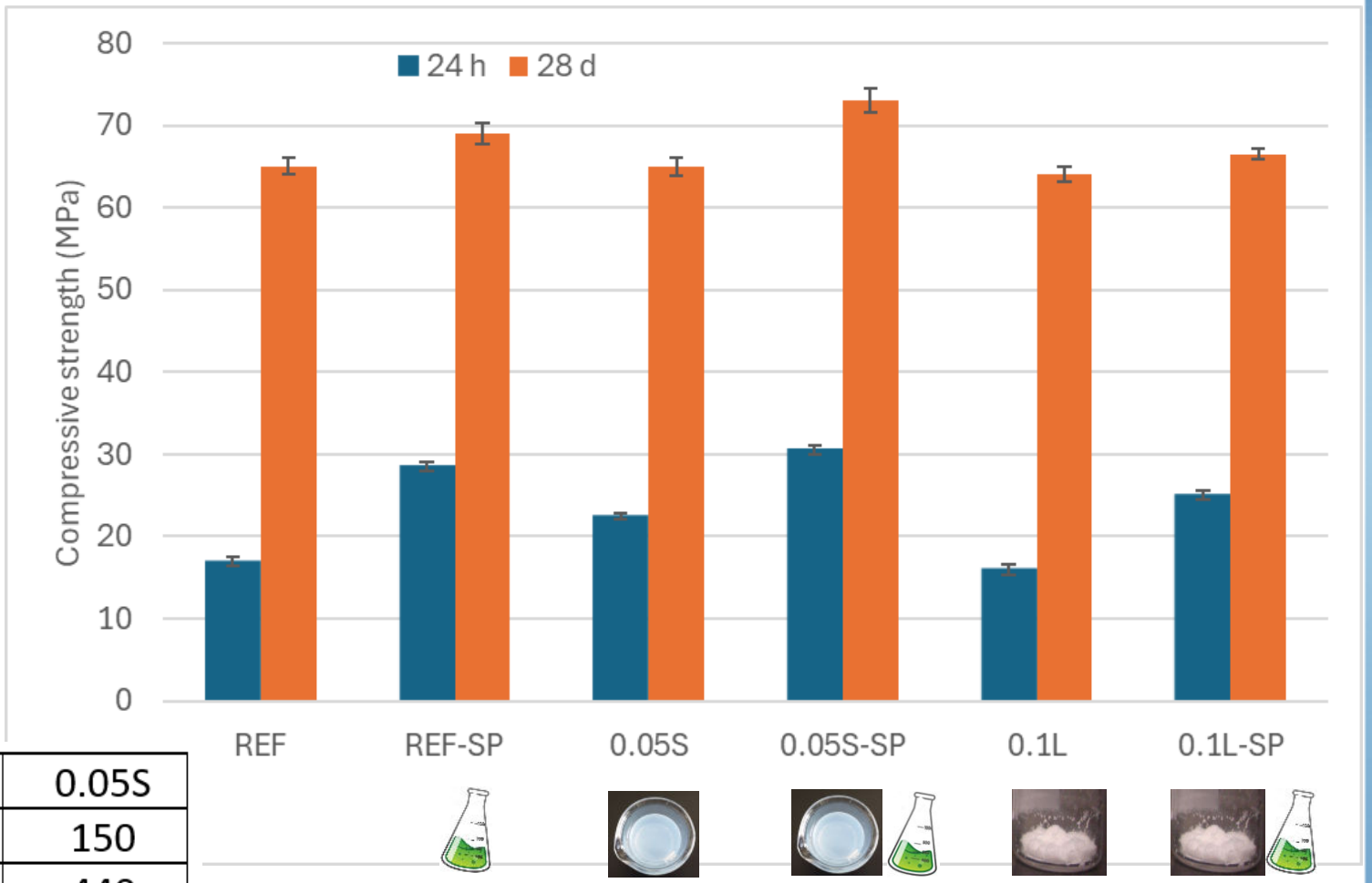


EN 1015-3

Effect of CNC on mortar performance

Effect on compressive strength

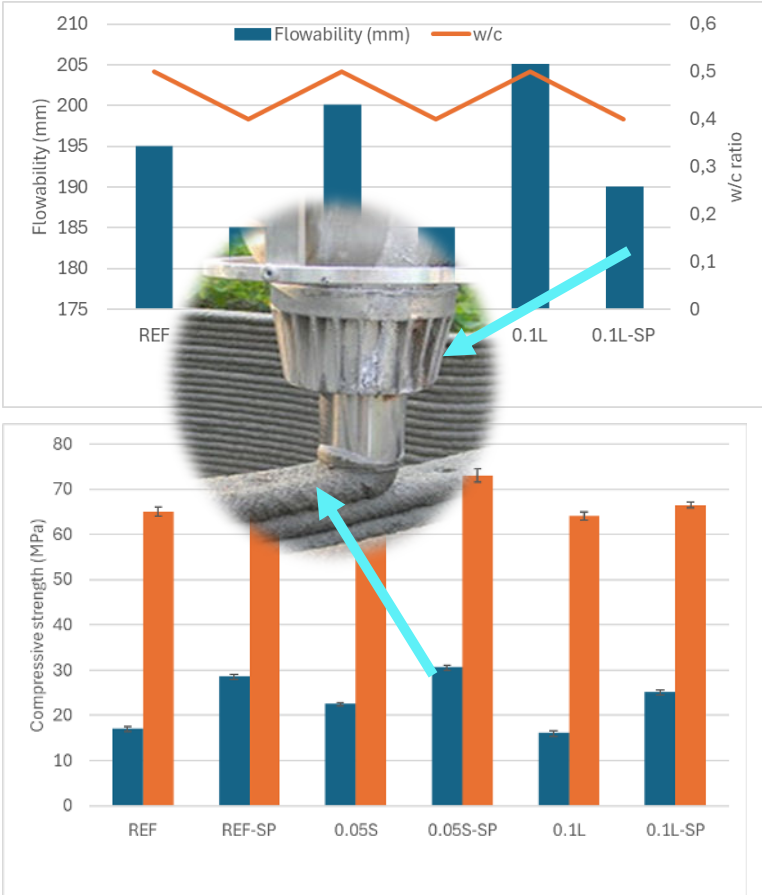




Setting time (s)	REF	0.05S
Initial	160	150
Final	440	440

Conclusions

- CNC induces stable cement dispersions, avoiding cement aggregation at low shear forces.
- CNC combined with SP helps to stabilize the cement dispersion.
- CNC increases water demand but, when it is combined with SP
  - ➔ constant low water demand
  - ➔ increase flowability of cement
  - ➔ increase compressive strength



Conclusions

Homogeneous mix

Non-stop process

Easy flow through the nozzle
High workability

↓

Dispersibility
Fluidity
Slow hydration

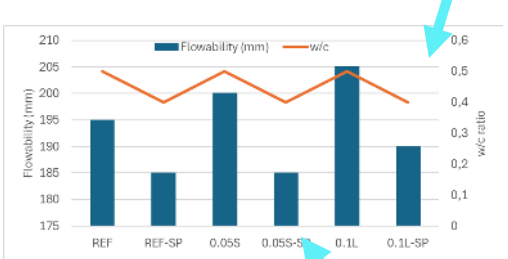
Self-supporting layers

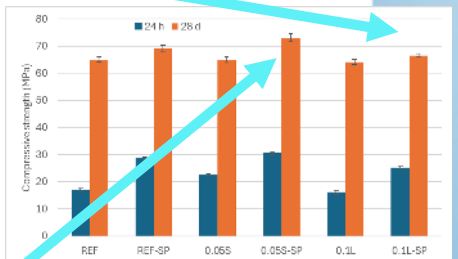
Fast development of compressive strength

↓

Aggregation
Low fluidity
Fast hydration

➔ Lyophilized CNC combined with SP but….with a little sacrifice of compressive strength





➔ CNC in suspension combined with SP but …. keeping constant the flowability of cement.

CNC as a biodegradable aid in 3D printing of cementitious materials

C. Negro, R. Jarabo, E. Fuente, P. Carballosa, JL García, A Blanco

ablanco@ucm.es

Acknowledgments

CDTI [SNEO-20181016, NEOTEC program)

Spanish Economy and Competitiveness Ministry: (CTQ2017-85654-C2-2-R)