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ZAVOD ZA GRADBENIŠTVO SLOVENIJE

SLOVENIAN NATIONAL BUILDING AND CIVIL ENGINEERING INSTITUTE

33. Conference
Rheology of Building Materials
Regensburg, 28th of February 2024

Cement paste as multiphase (non)colloidal particulate dispersion and its viscoelastic rheological behaviour

Cement paste is mostly regarded as non-Newtonian fluid and its liquid-like behaviour described with Bingham model obtained from flow curve. This simplified consideration of cement paste is adequate for conventional use of material, nevertheless employment of novel chemical admixtures, supplementary materials, and casting technologies expanded the set of properties required for characterization. In addition to viscosity, elasticity is essential for modern cementitious materials. The paper/presentation will discuss the rheometry protocols and equipment and their significance in thorough characterization of fresh cementitious materials. Impact of recovery time, surface smoothness and shear rate will be shown and explained through physical and chemical processes occurring in the material.

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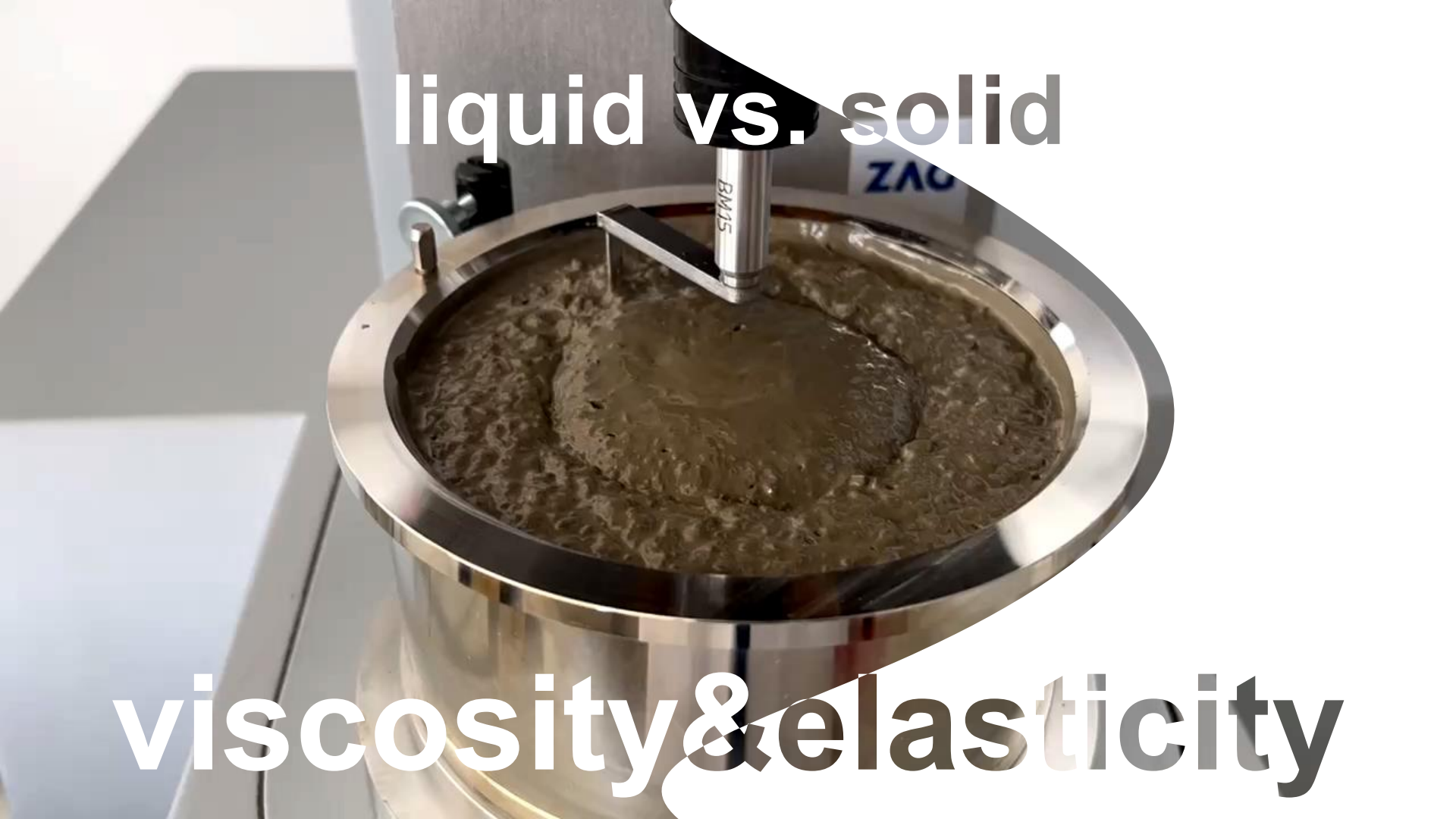
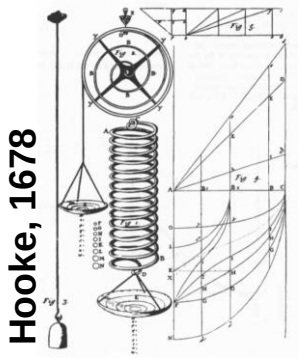
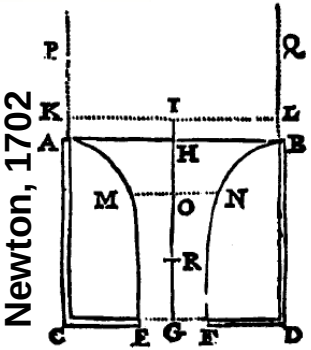

liquid vs. solid
viscosity&elasticity



Hooke

G,τ



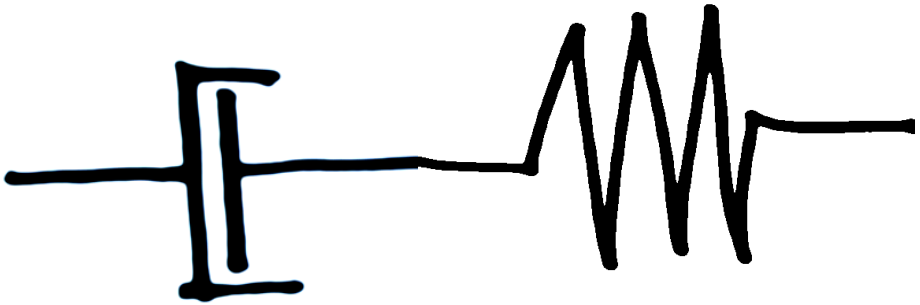
Newton

(Stokes)

η,τ

Setting Hardening

Initial state t_i → Final state t_f



$$\eta(t) \leqslant G(t)$$

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Viscous

Elastic

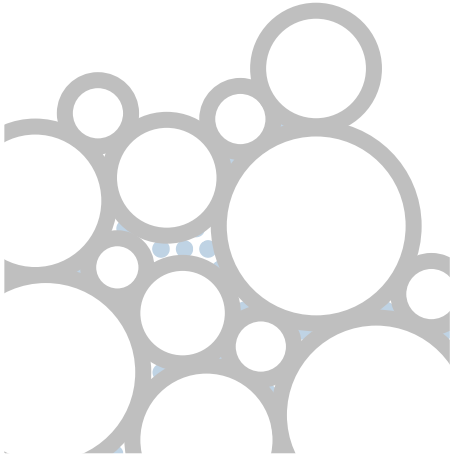
why

- decreased workability
- better stability
- shape retention
- degree of aggregation/clustering of particles,
- impact of admixtures (mineral or chemical)

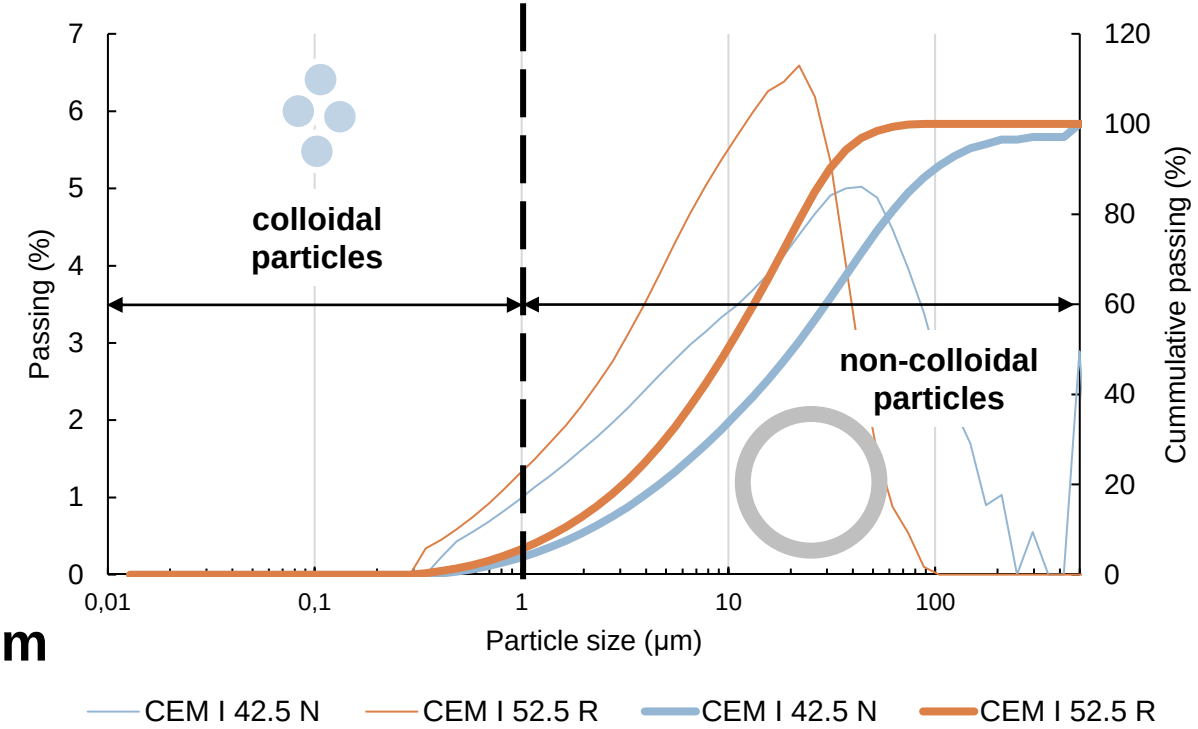
Particulate suspension/gel

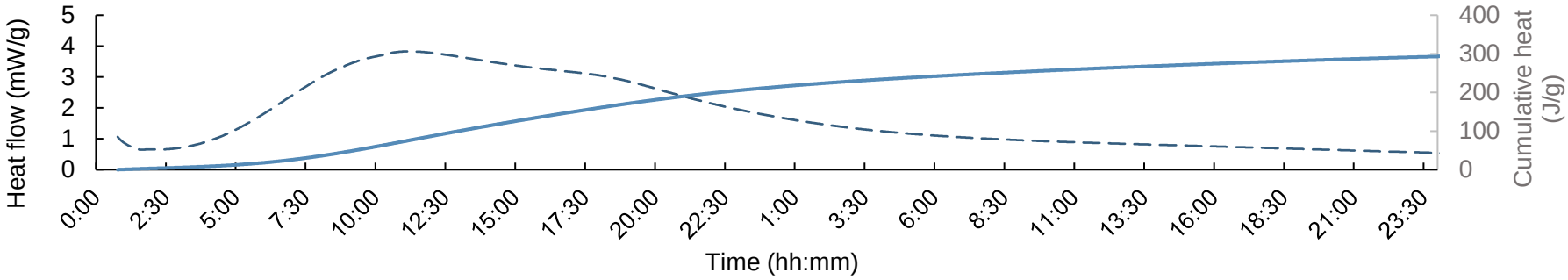
- **multiphase liquid** (solid particles in liquid medium): dilute and dense
- the rheological response and (gel) elasticity are direct functions of the **particle volume fraction**
- biggest concern (since ancient times): **STABILITY**
- particles, larger than about 1 μm tend to **settle under gravity** unless the particle density matches that of the suspending medium, or the suspending medium is very viscous
- small particles are maintained in suspension by **Brownian motion**
- particle collisions often leads to **aggregation**, followed by **gelation** or **gravitational settling**

Cement paste/mortar/concrete



Cementitious system

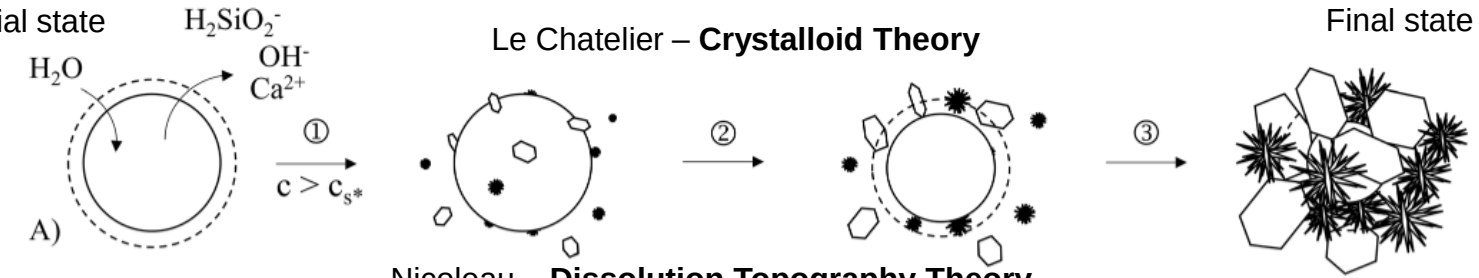




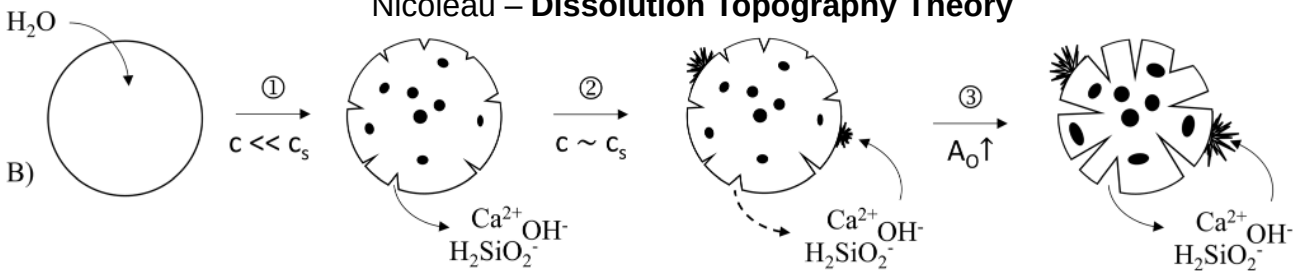
t_i — Setting — Hardening — t_f

Initial state — Final state

1906 — Le Chatelier – **Crystalloid Theory**



2016 — Nicoleau – **Dissolution Topography Theory**



John, E., Lothenbach, B. J Mater Sci (2023) 58. 10.1007 / s10853-023-08651-9

Rheology of particulate suspensions/gels

problems

- Poor reproducibility
- Sensitivity to suspension/gel preparation
- Sensitivity to shear history
- Extremely limited range of linear viscoelastic response
- Slip

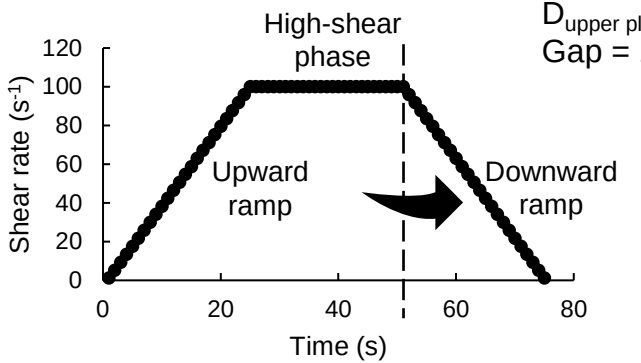
RECOVERY TIME

SURFACE ROUGHNESS

SHEAR RATE

Recovery time

FLOW CURVE
Kinematics

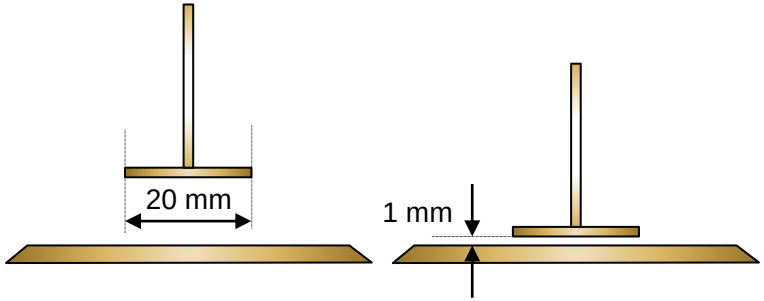


Material&mixture

w/c = **0.5**
CEM I 52.5R Salonit Anhovo

AntonPaar MCR 302
Plate-plate (serrated) geometry

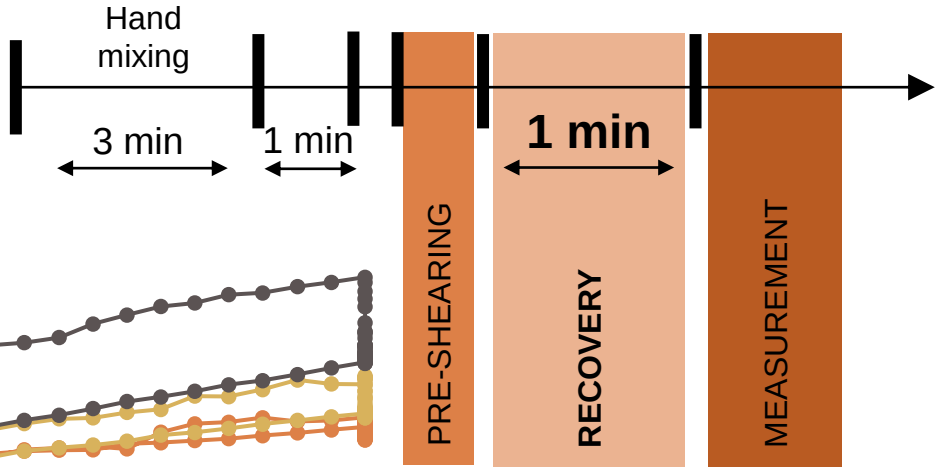
$D_{upper\ plate}$ = 2 cm
Gap = 1 mm

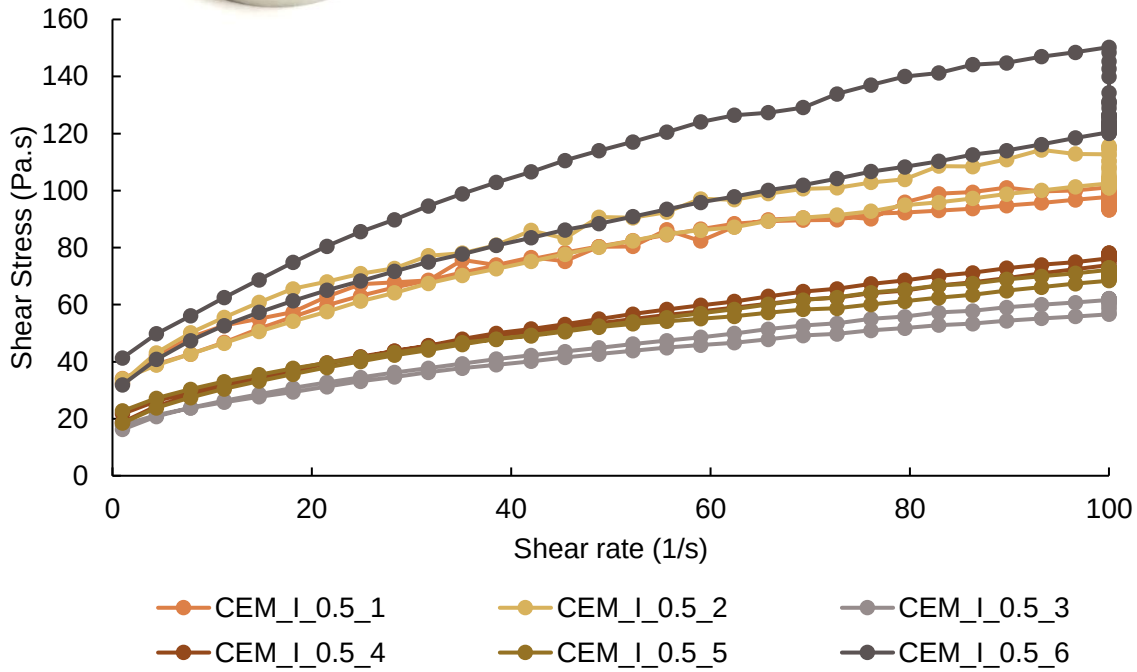


Recovery time

Testing geometry

Testing protocol





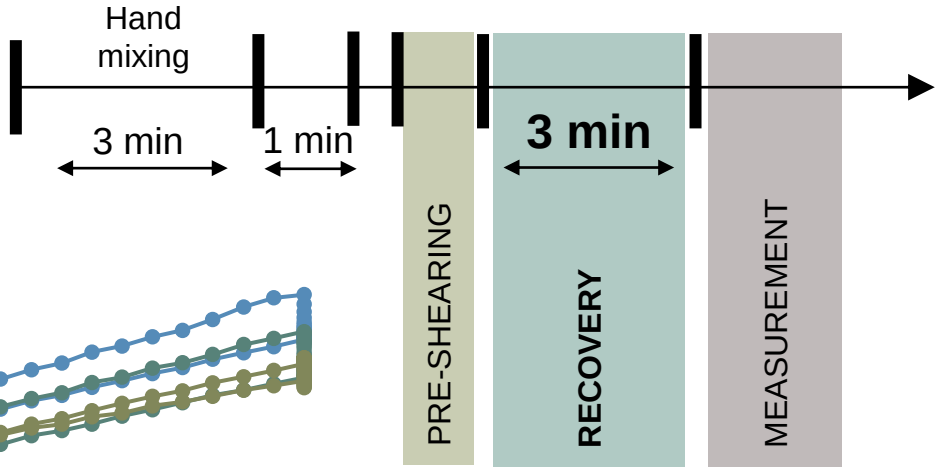
Sample preparation

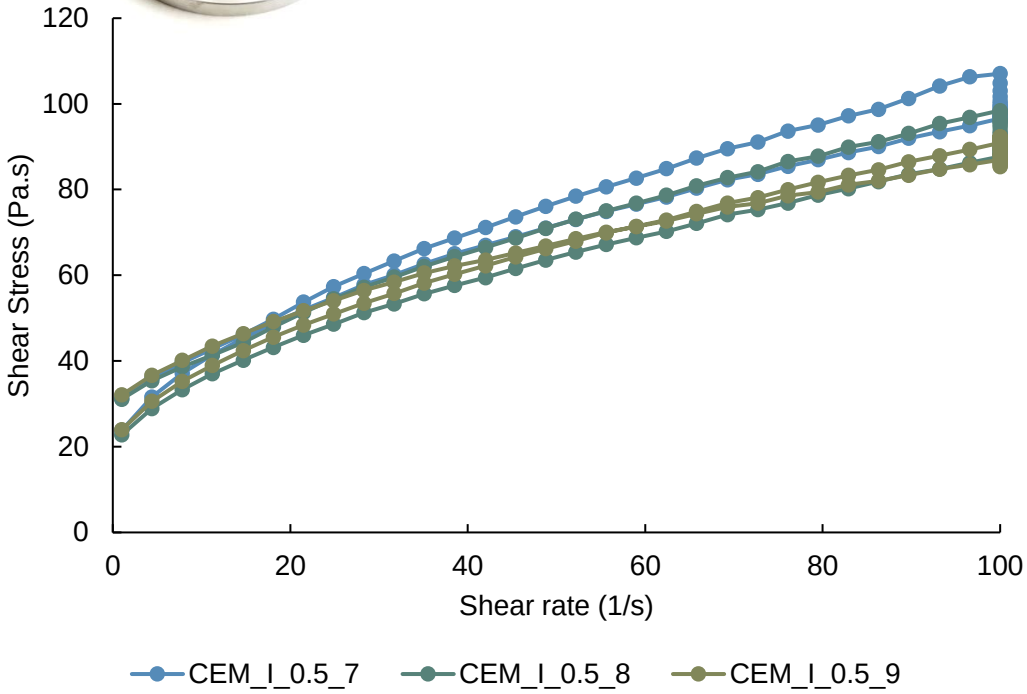
Weight = 10 g
6 series
T = 20 °C
CEM I 52.5R
w/c = 0.5

Recovery time

Testing geometry

Testing protocol



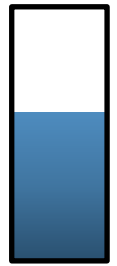


Sample preparation

Weight = 10 g
3 series
T = 20 °C
CEM I 52.5R
w/c = 0.5

Bingham model

Recovery time

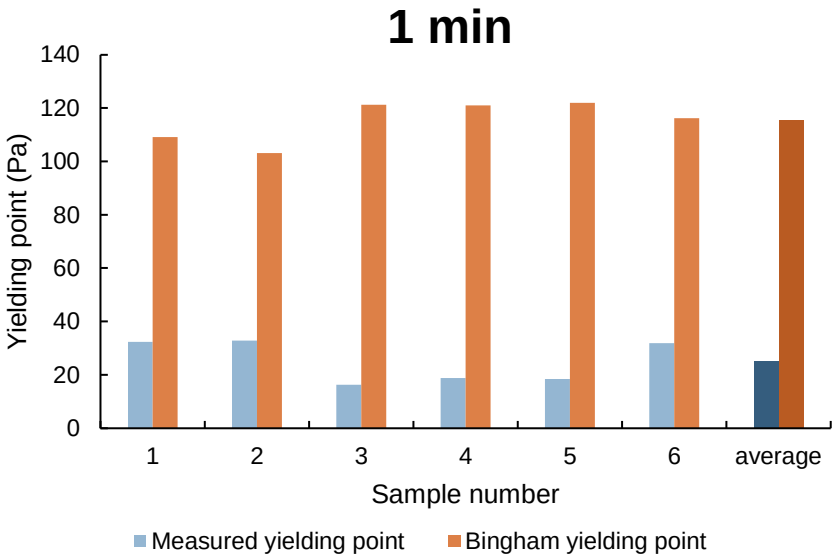


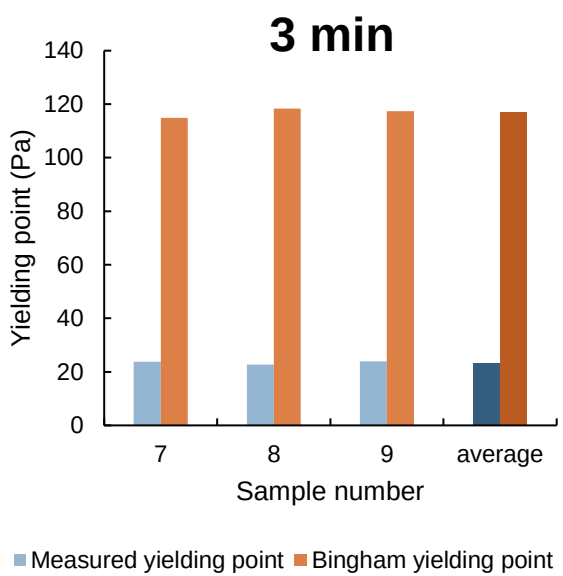
OTHER CURVE FITTINGS

Casson model
Herschel-Bulkley model
Windhab model
Tscheuschner model
Polynomials (Williamson, Rabinowitsch, Weissenberg)

$$\tau = \tau_B + \eta_B \cdot \dot{\gamma}$$

Recovery time



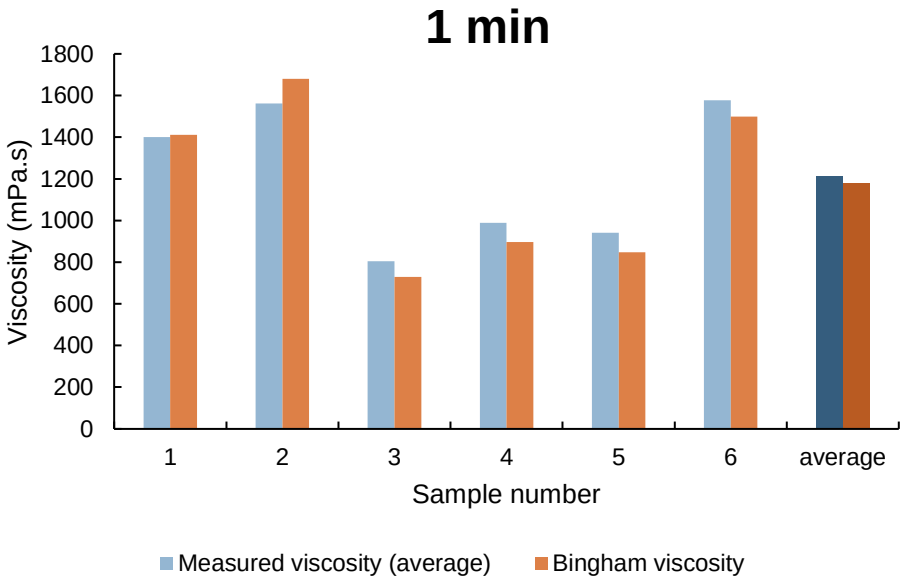


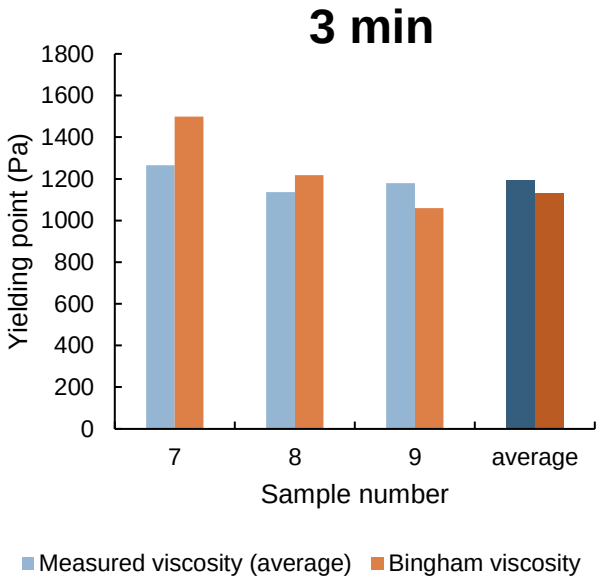
X = 25,08 / 115,45
σ = 8,01 (31,9 %) / 7,74 (6,70 %)

X = 23,50 / 116,86
σ = 0,64 (2,72 %) / 1,74 (1,49 %)

YIELDING POINT

Recovery time





X = 1212,6 / 1177,6
σ = 340,7 (28,1 %) / 399,6 (33,9 %)

X = 1193,6 / 1128,8
σ = 65,6 (5,5 %) / 222,5 (19,7 %)

VISCOSITY

Recovery time

- Prolonged recovery time helps improving reproducibility
- Recovery time could be regarded as „property“ of the mixture – the time in which structure roughly builds (structuration)
- Bingham model drastically overestimates yielding stress – why not use measured/calculated values?

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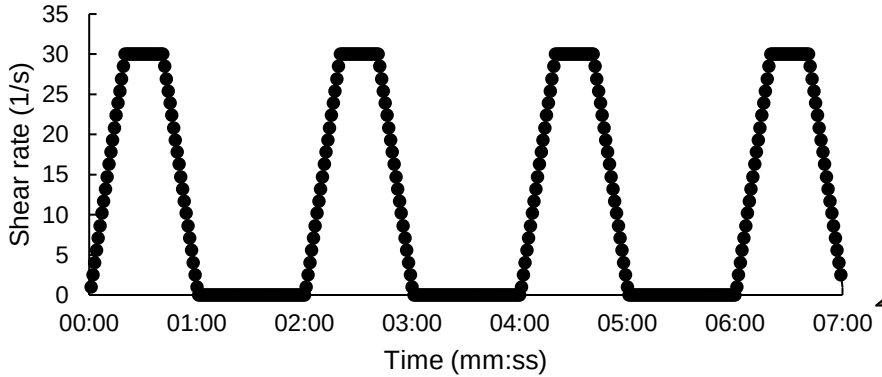
Surface roughness

FLOW CURVE
Kinematics



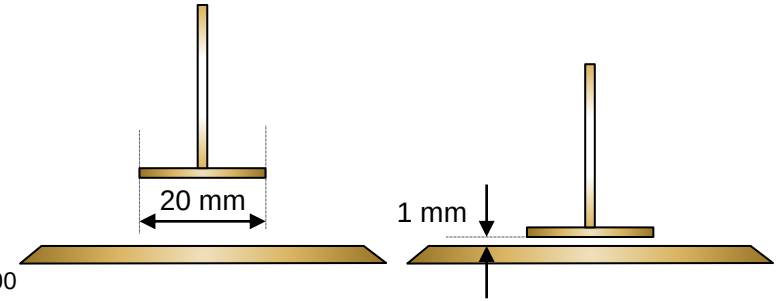


Plate-plate geometry:
- **serrated**
- **smooth**
- **sandpaper (P60)**

$D_{upper\ plate}$ = 2 cm
Gap = 1 mm

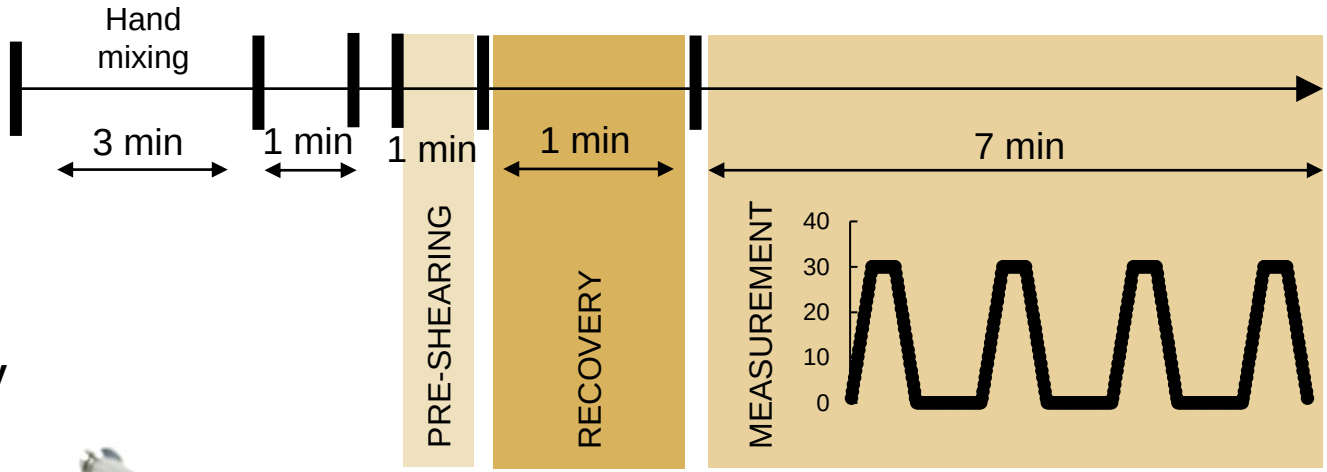
AntonPaar MCR 302

Material&mixture

v/c = **0.4**
CEM I 52.5R Salonit Anhovo

Surface roughness

Testing protocol

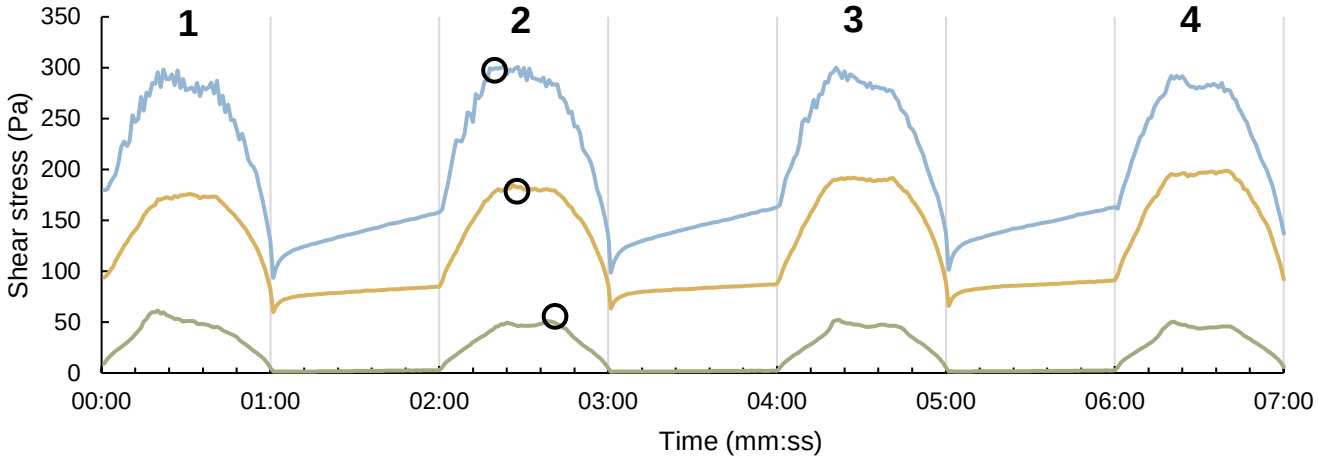


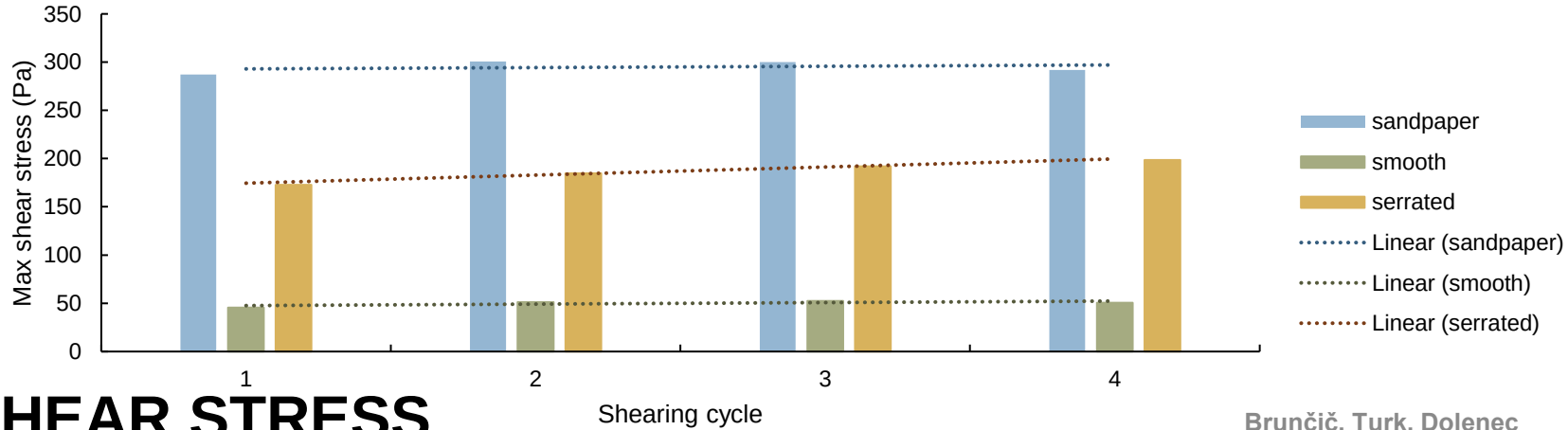
Testing geometry

Sample preparation

Weight = 10 g
1 series
T = 20 °C
CEM I 52.5R
w/c = 0.4

Surface roughness





SHEAR STRESS

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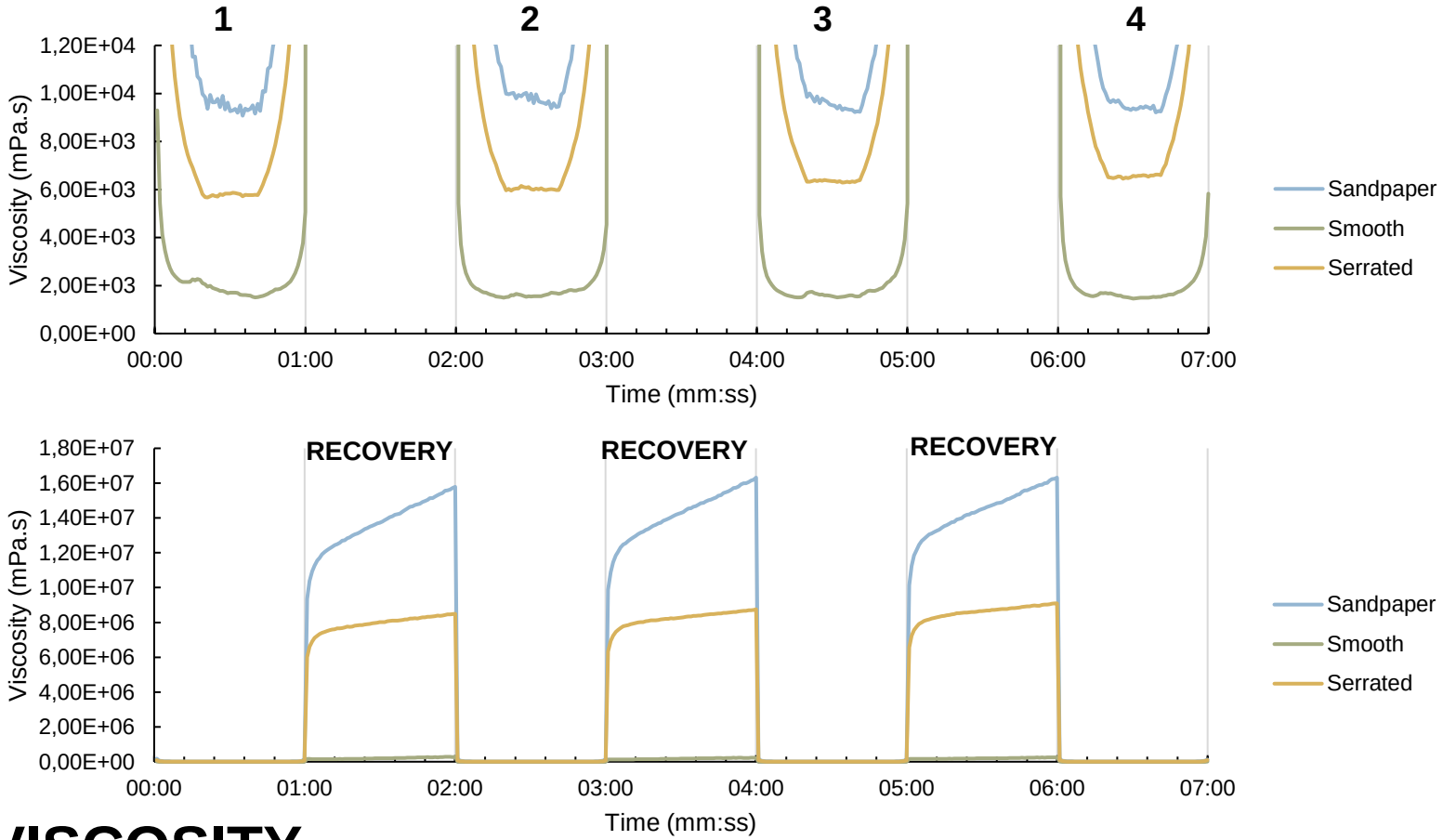
Cement paste as multiphase (non)colloidal particulate dispersion and its viscoelastic rheological behaviour

Surface roughness



VISCOSITY

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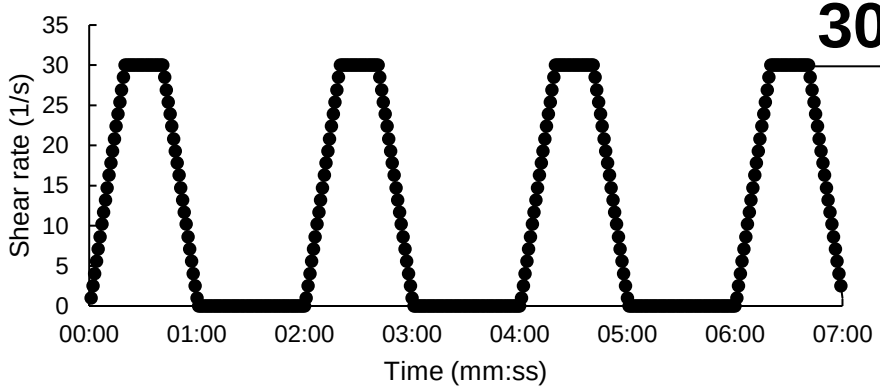
Cement paste as multiphase (non)colloidal particulate dispersion and its viscoelastic rheological behaviour

Surface roughness

- Values obtained in measurements are highly dependent on geometry surface smoothness/roughness
- Use of geometry with rougher surface results in higher shear stresses and viscosities,
- **finer irregular coarseness** (sandpaper) seems to **provide highest sensitivity (question of sample height!)**
- Slip is apparent on smooth surface even at low shear rates – it can be identified with „loss“ of correlation between shear rate and shear stress/viscosity

Shear rate

FLOW CURVE
Kinematics



30 / 80 / 240 (1/s)

... (50 cycles)

Vane probe geometry:
- Diameter 22 mm
- Length 40 mm

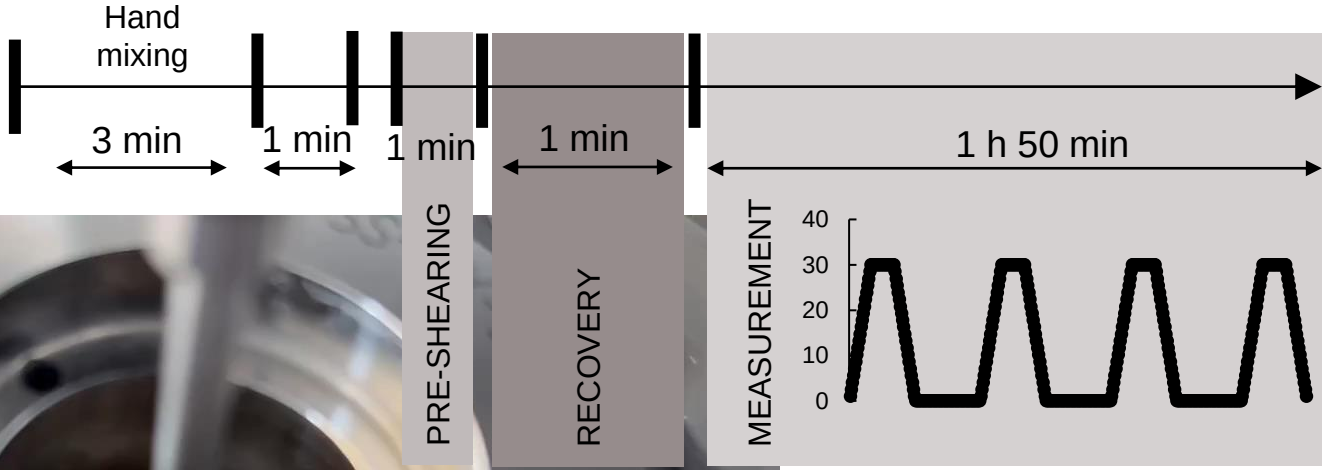
Cup geometry:
- Inner diameter: 39 mm

Material&mixture

w/c = **0.5**
CEM I 52.5R Salonit Anhovo
9 wc % diatomaceous earth

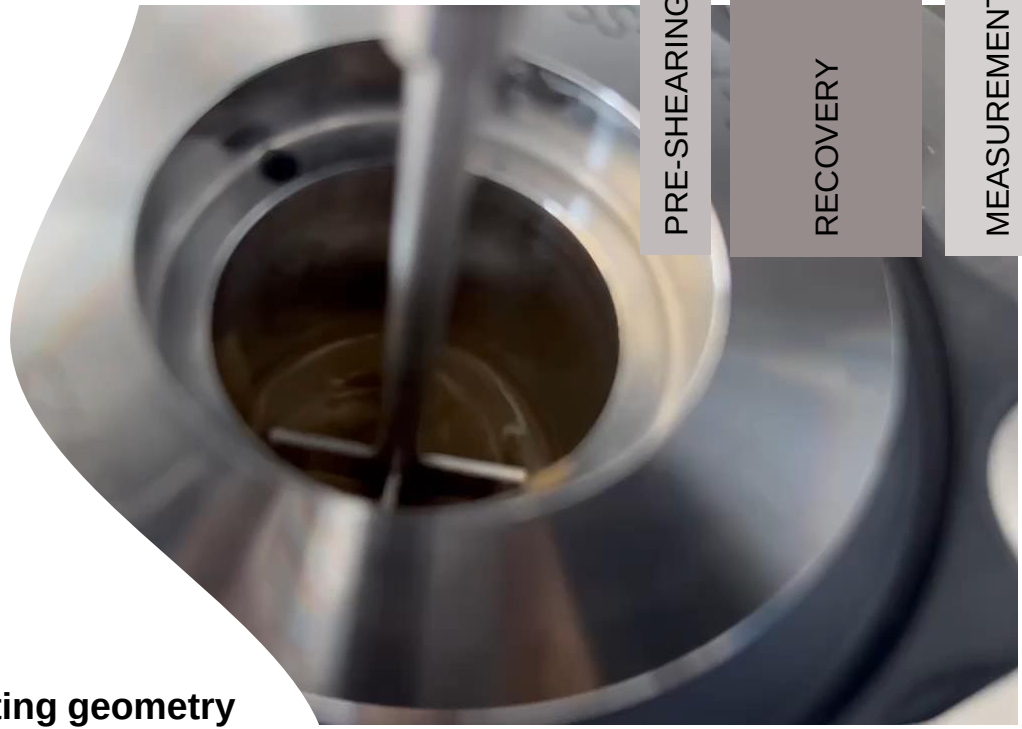
AntonPaar MCR 302

Testing protocol



Shear rate

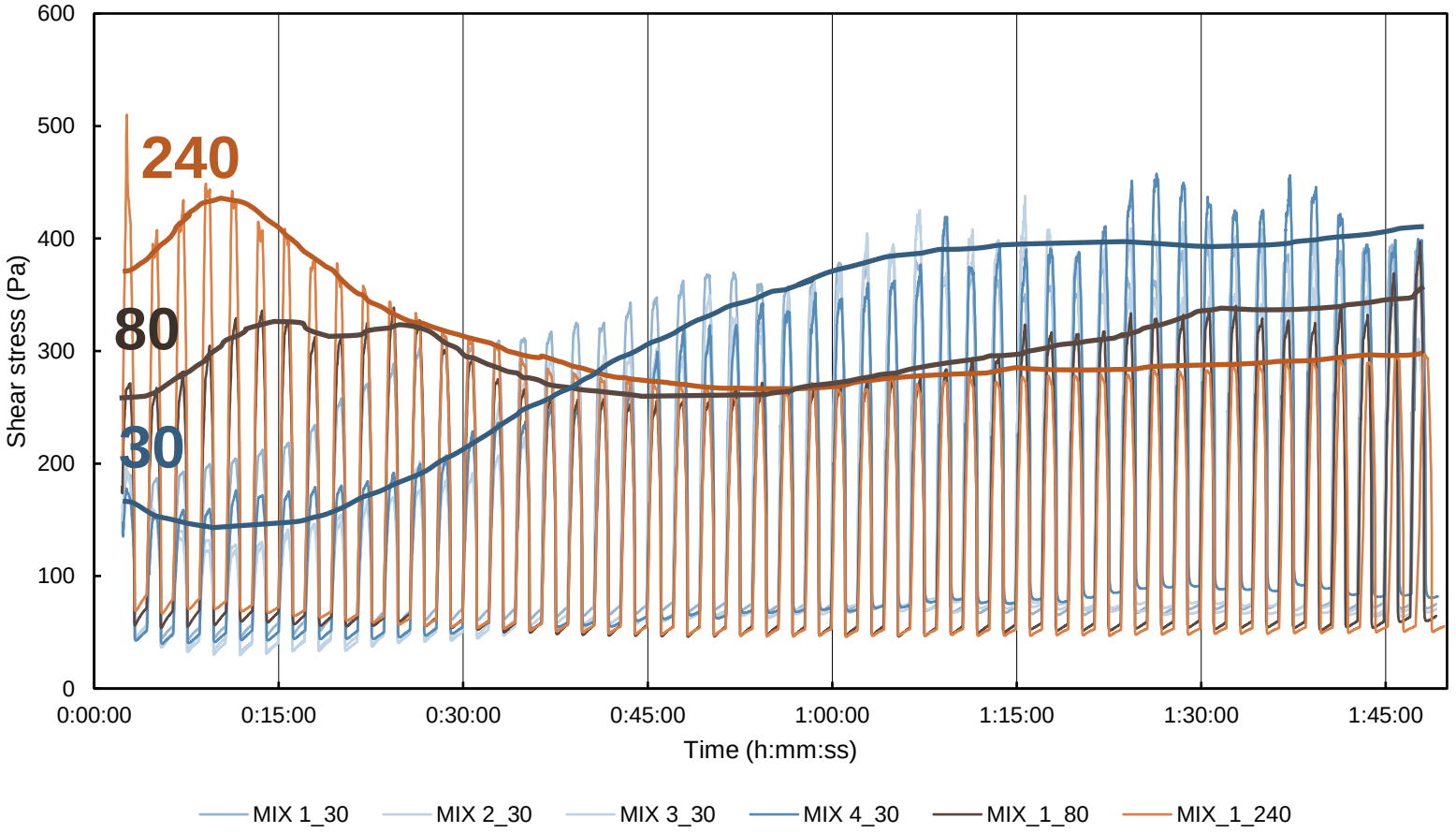
Testing geometry



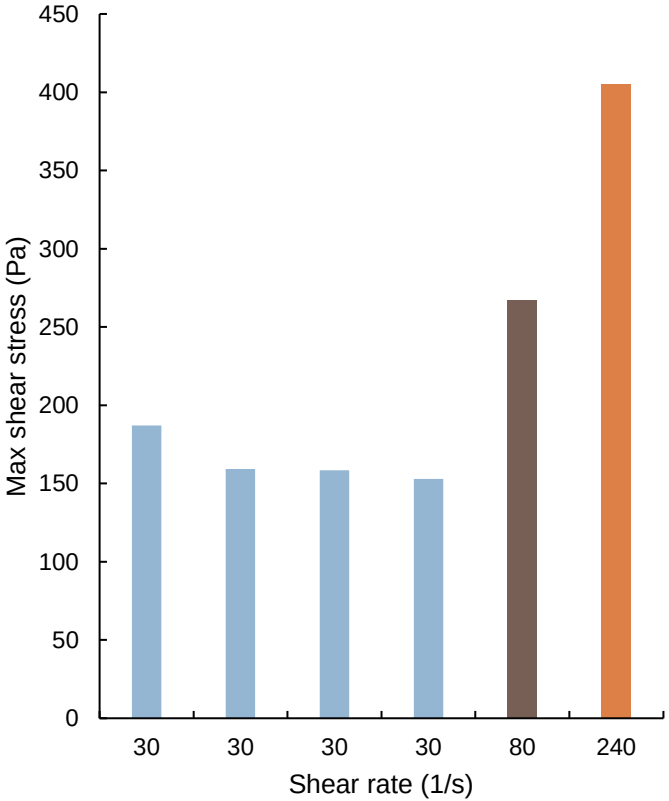
Sample preparation

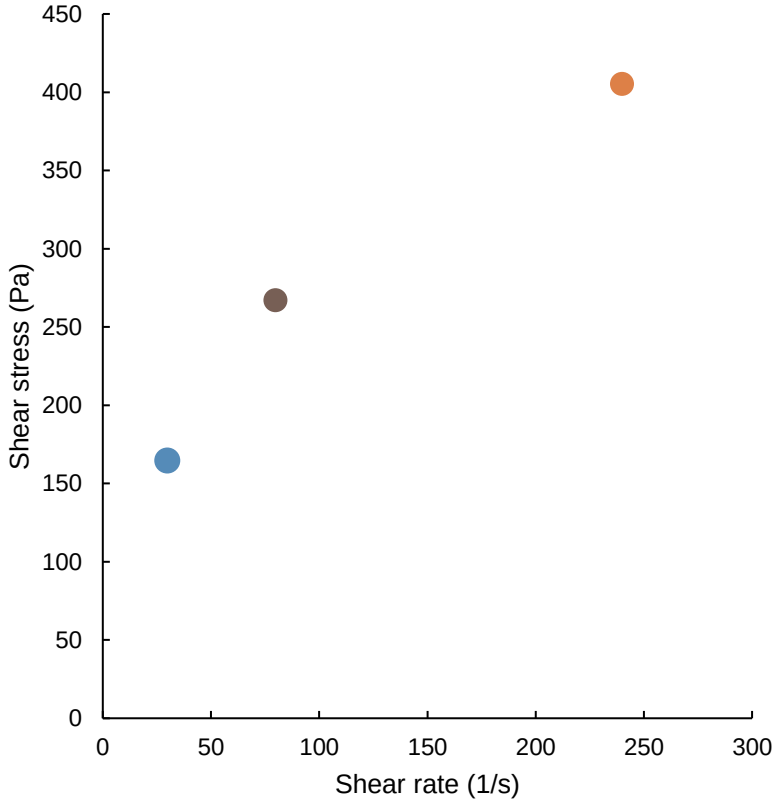
Weight = 100 g
1 (4) series
T = 20 °C
CEM I 52.5R
Diatomaceous earth
w/c = 0.5

Shear rate


240
80
30
Shear stress (Pa)
600
500
400
300
200
100
0
0:00:00
0:15:00
0:30:00
0:45:00
1:00:00
1:15:00
1:30:00
1:45:00
Time (h:mm:ss)
MIX 1_30
MIX 2_30
MIX 3_30
MIX 4_30
MIX_1_80
MIX_1_240

Shear rate


Max shear stress (Pa)
450
400
350
300
250
200
150
100
50
0
30
30
30
30
80
240
Shear rate (1/s)


Shear stress (Pa)
450
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Shear rate (1/s)

Shear rate

- Cementitious materials are shear rate-dependent – the correlation is not linear
- Constant mixing at various shear rates has impact on viscous behaviour and structural recovery of cementitious materials:
  - use of higher shear rates tends to result in higher shear stresses with pronounced peak in first cycles, but then values drop and remain constant
  - use of lower shear rates results in lower shear stresses in first cycles, values then start to increase and stabilise (effect of sedimentation?)

Acknowledgment

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Thank you for your attention.