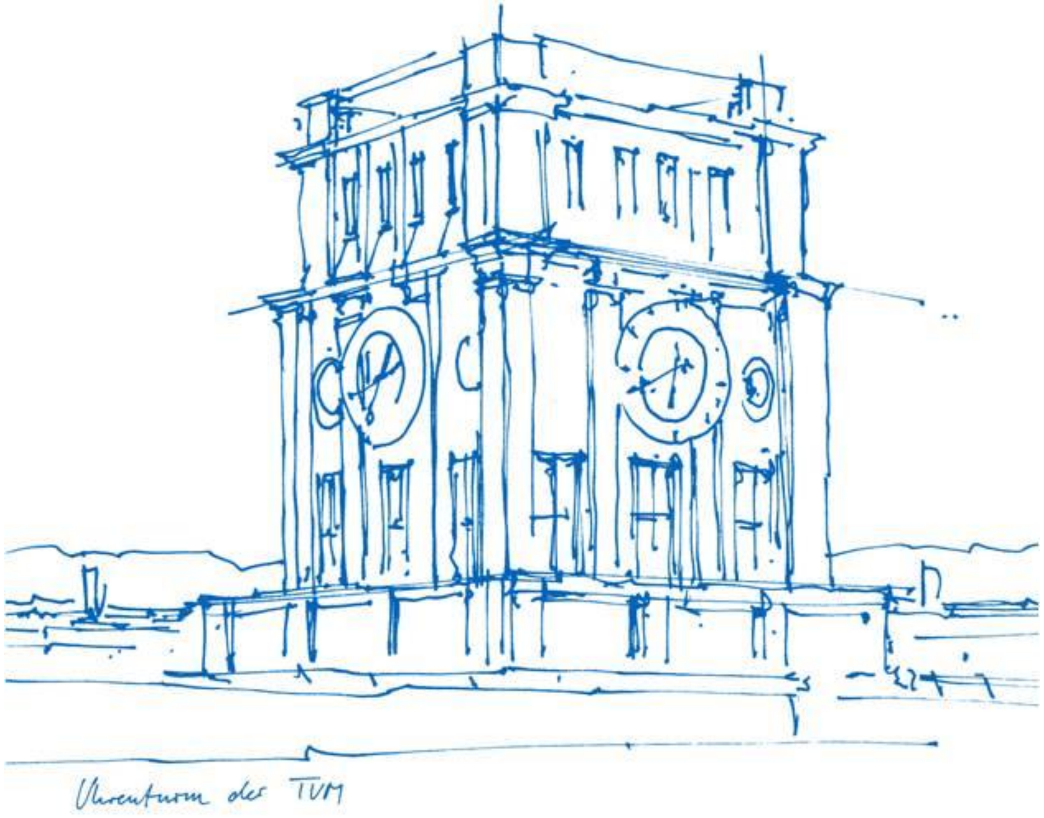
Comparative small and large gap rheometry for cementitious pastes



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Centre for Building Materials (cbm)

28.02.2024 – 33. internationale Konferenz

"Rheologische Messungen an mineralischen Baustoffen"

Motivation – Analysis of non-Newtonian rheology

Standard concrete

Viscoplastic flow

Rest – Yield stress – Flow

Compare CONCERA® control flow concrete with conventional mix designs - YouTube

Advanced mixtures

Thixotropic viscoelastoplastic flow

Rest – Viscoelasticity Thixotropy – Flow

Sphinx HE20A - Ultra-High Performance Concrete - YouTube

- Mixtures with high amounts of ***additives*** and ***admixtures*** change rheology from ***viscoplastic*** to ***viscoelastoplastic*** with ***thixotropic*** behavior

Motivation – Analysis of non-Newtonian rheology

Microstructural rheology

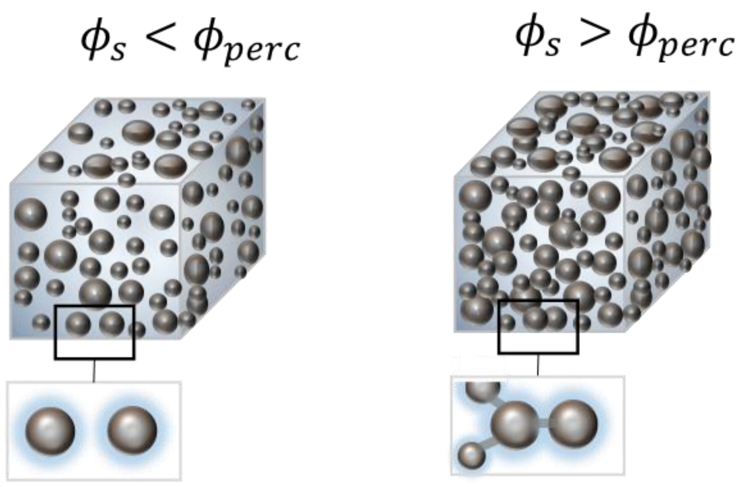
- Cementitious pastes are colloidal suspensions with interparticle forces beyond a packing density threshold Φ_{perc}

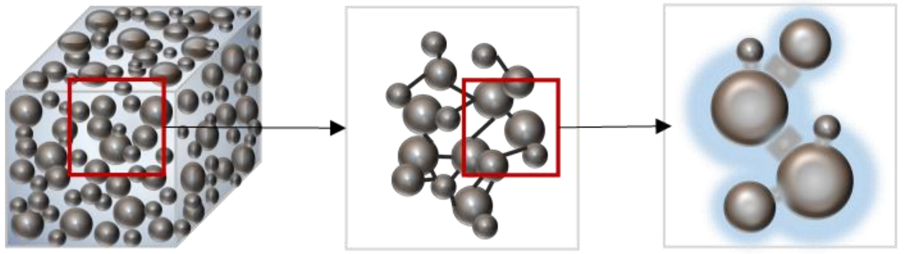
$$\phi_s = \frac{V_s}{V_\Sigma}$$

- With increasing packing density, particles agglomerate at rest and low shear rates

- With increasing packing density, ***viscosity η*** increases (Krieger-Dougherty model)

$$\frac{\eta}{\eta_0} = 1 - (\frac{\phi_s}{\phi_m}^{-[\eta]\phi_m})$$

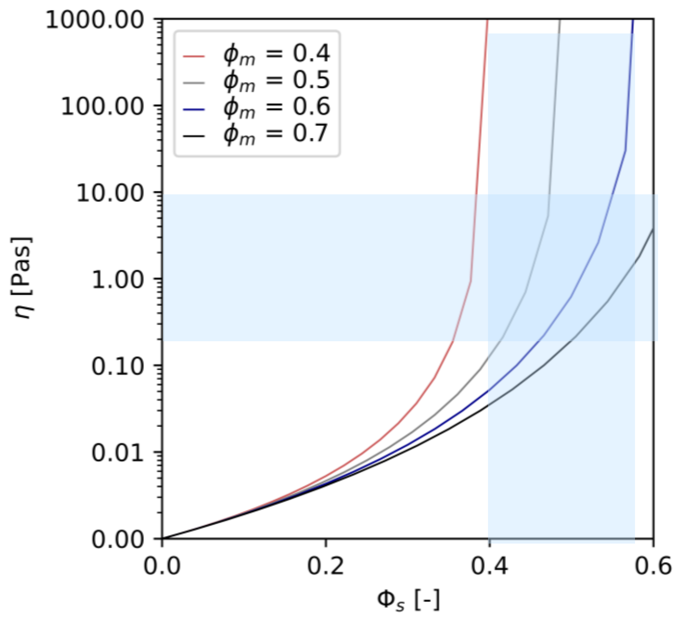




Motivation – Analysis of non-Newtonian rheology

Microstructural rheology

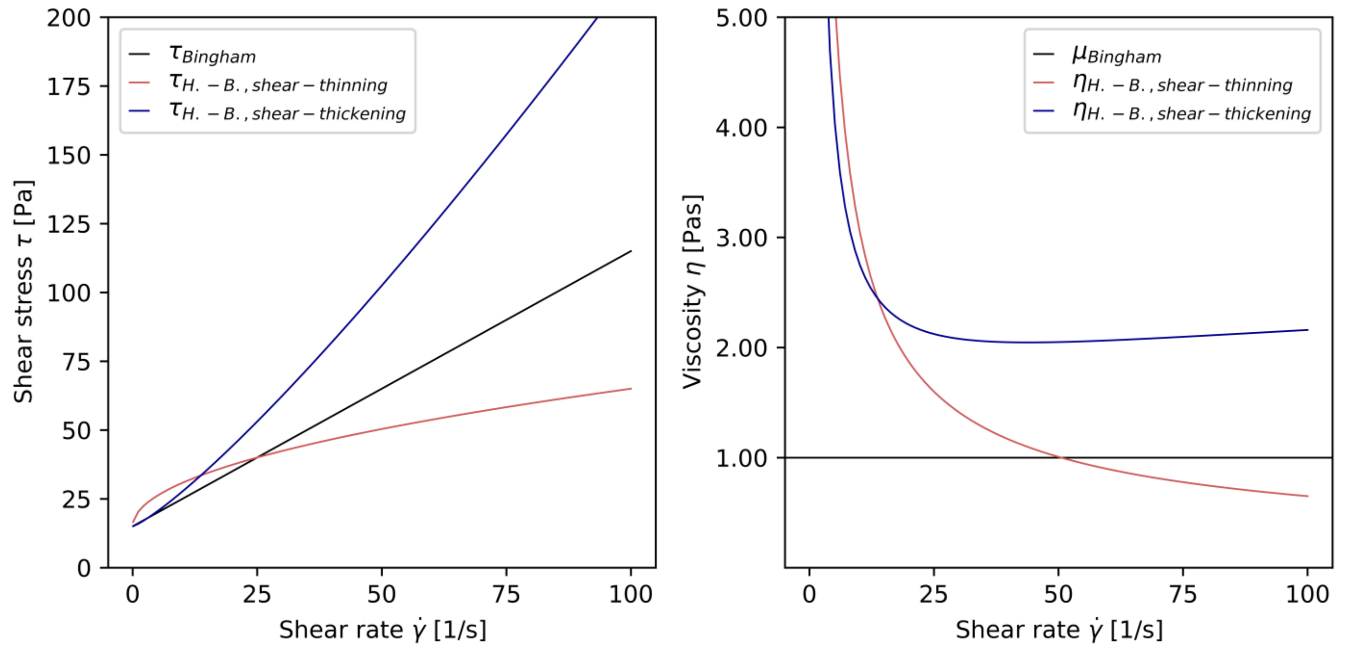
$$\frac{\eta}{\eta_0} = 1 - \left(\frac{{\phi_s}^{-[\eta]\phi_m}}{\phi_m}\right)$$



(b)

Phenomenological modeling of non-Newtonian flow

$$\tau = f(\eta(\phi_s); \dot{\gamma})$$



Motivation – Rheometric measurements

Absolute rheometric measurements

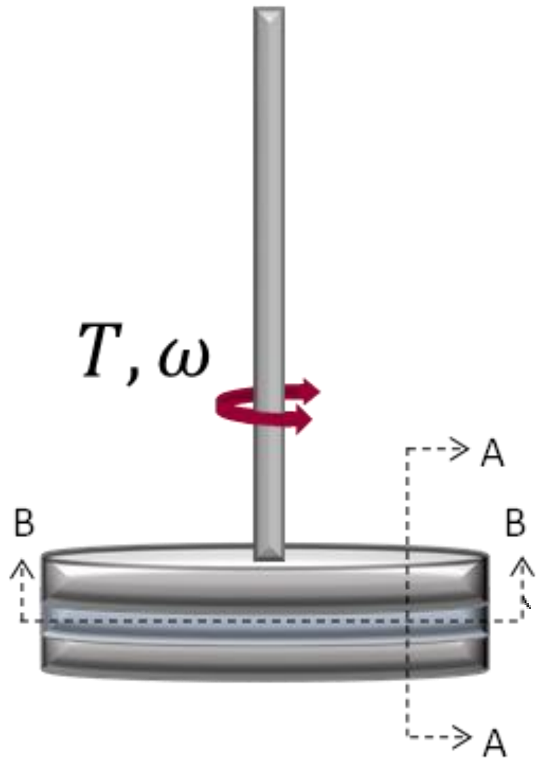

- Small gap: homogeneous shear field is assumed
  - ➢ Rheological data are directly calculated from device raw data
- Examples:
  - ➢ Parallel plates
  - ➢ Coaxial cylinders
  - ➢ Cone and plate system
- Drawback: no large particles can be measured

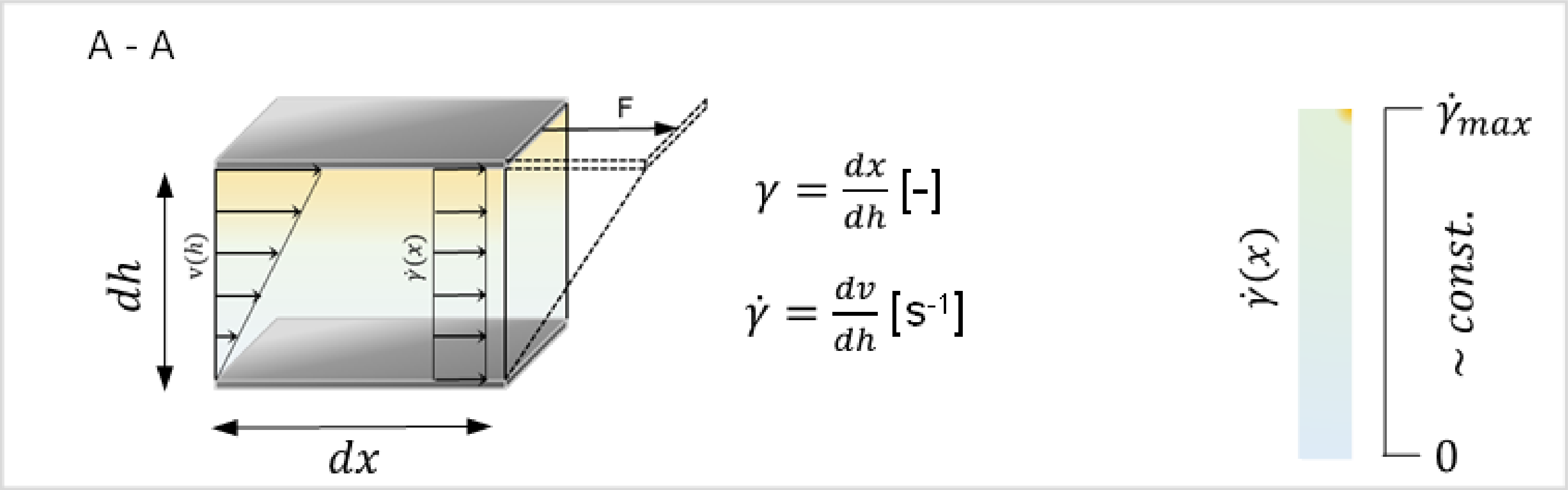

Relative rheometric measurements

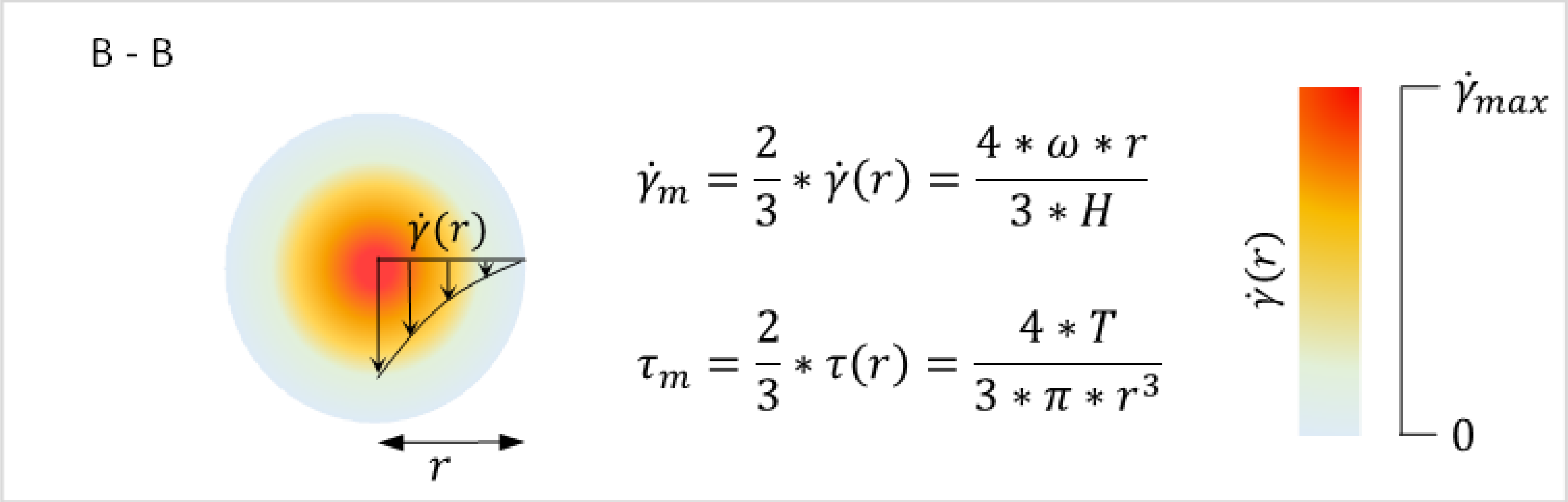
- Large gap: heterogeneous shear field
  - ➢ Rheological data cannot be directly calculated from device raw data
  - ➢ Approximation equations required
- Examples:
  - ➢ Vane-in-Cup
  - ➢ Coaxial cylinders
  - ➢ Searle or Couette
- Large particles can be measured

➢ But are the measured rheological properties of cementitious pastes from the different systems comparable?

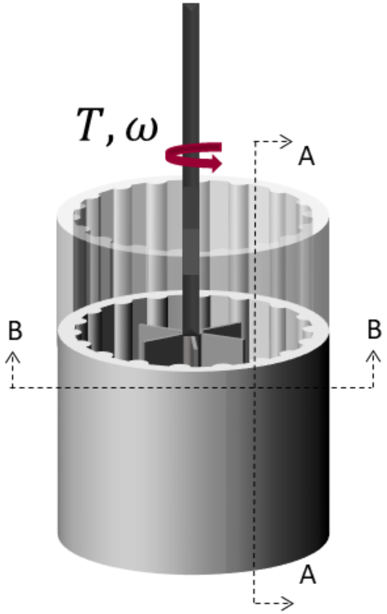
Rheometry: Fundamentals of absolute measurements

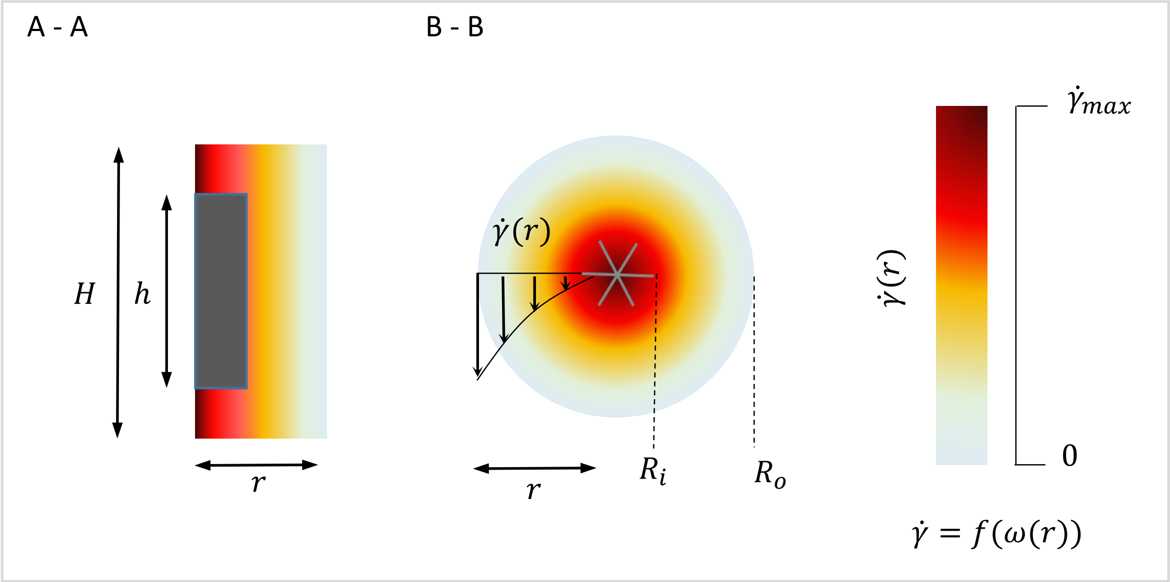


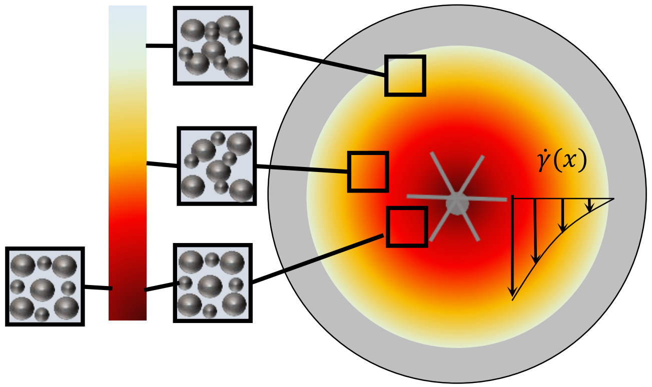




Rheometry: Fundamentals of relative measurements



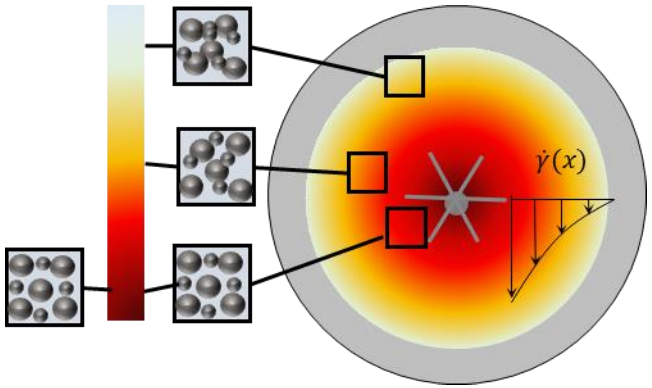




$$\tau_i = \frac{T}{2\pi h R_i^2} \; ; \; \tau_o = \frac{T}{2\pi h R_o^2}$$

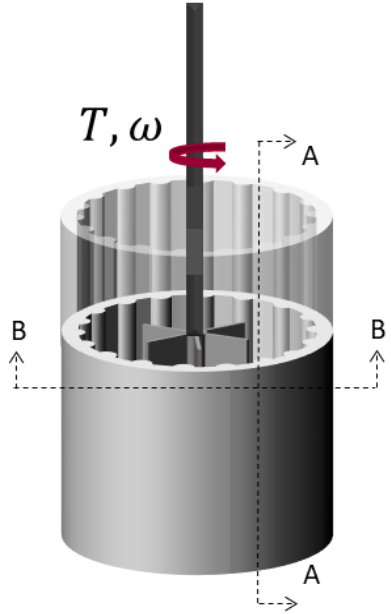
- Large gap: heterogeneous shear field
  - ➢ Rheological data cannot be directly calculated from device raw data
  - ➢ Approximation equations required

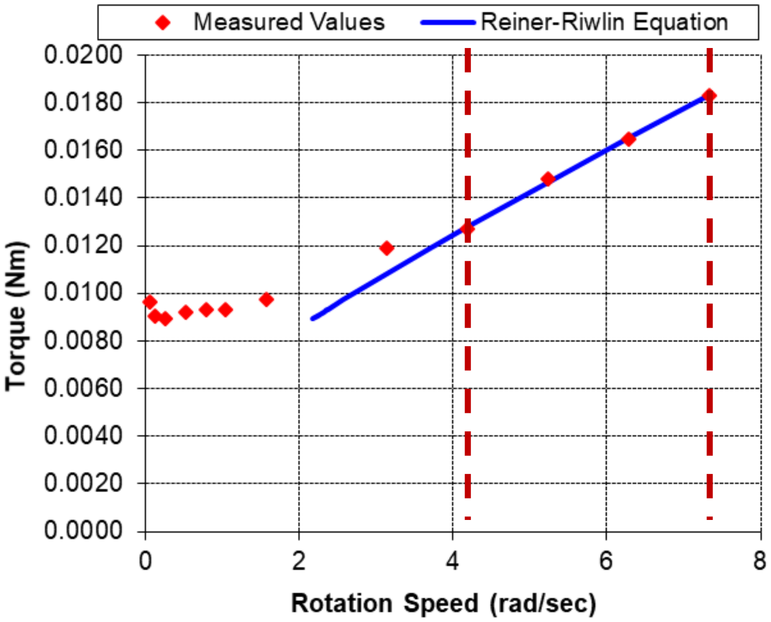
Rheometry: Fundamentals of relative measurements



$$\omega = \left(\frac{T}{4\pi h\mu}\right)\left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) - \left(\frac{\tau_{0,B}}{\mu}\right)\ln\left(\frac{R_o}{R_i}\right)$$

$$\tau(\dot{\gamma}) = \tau_{0,B} + \mu\dot{\gamma}$$



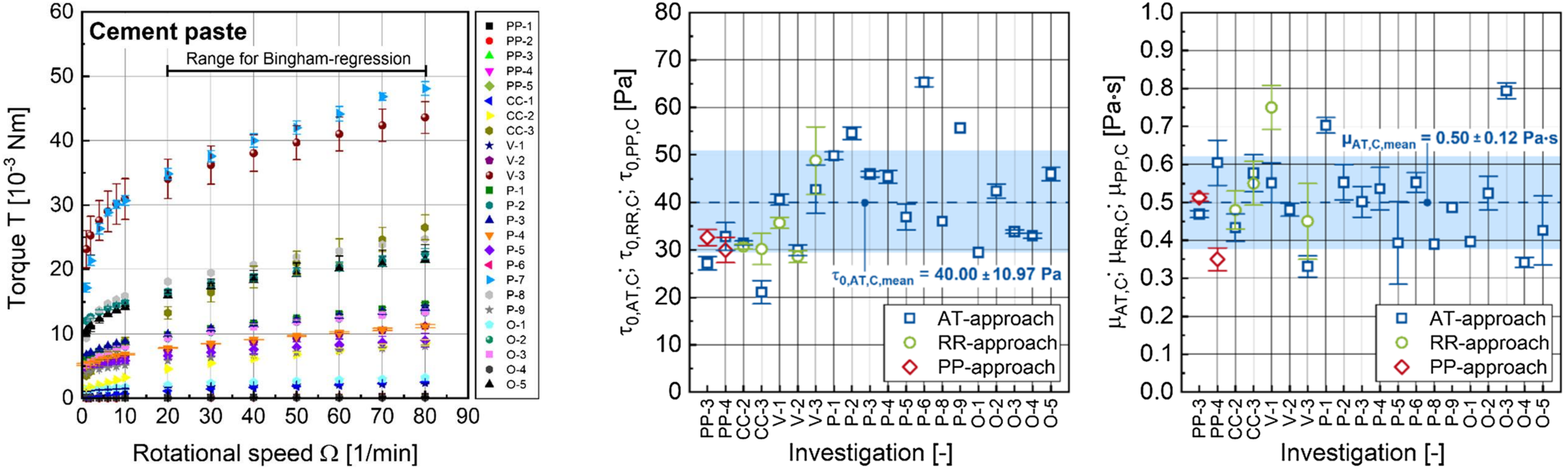


- Reiner-Riwlin equation correlates the device raw data to rheological parameters
- Rheological parameters describe a Bingham Fluid
- In this example, a certain range of rotational speed was chosen for the iterative fit

Research question:

To which extent are Parallel-Plate rheometry and Vane-in-Cup rheometry comparable?

Round robin test in research project



- Round Robin test on a cementitious paste with $\Phi_S = 0.45$
- Raw data of different rheometers T, ω converted to flow data $\tau, \dot{\gamma}$
- Or direct calculation of rheological parameters $\tau_0; \mu$

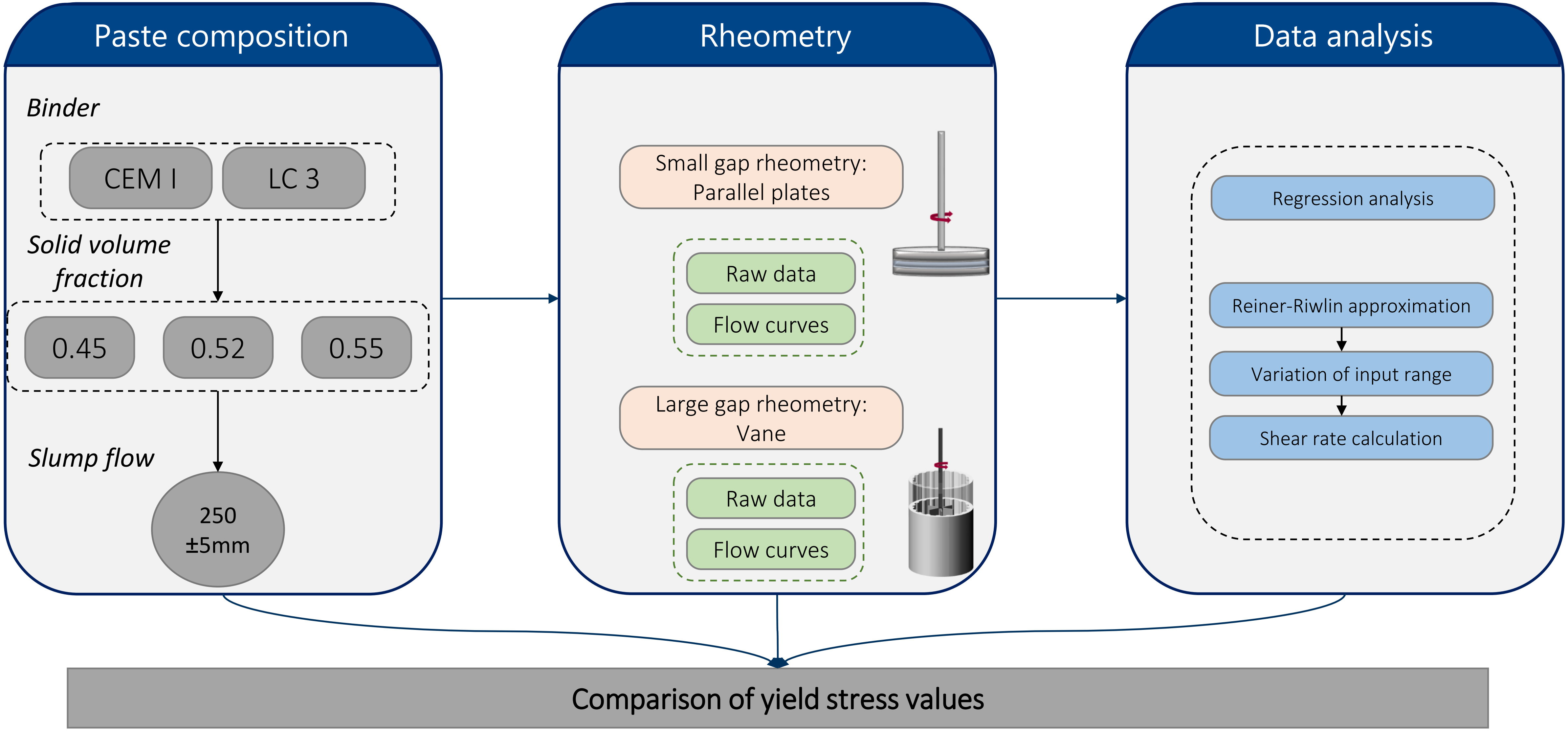
- Rheological parameters were calculated with different methods
- Coefficient of variation ~30%

Haist, M., Link, J., Nicia, D. et al. Interlaboratory study on rheological properties of cement pastes and reference substances: comparability of measurements performed with different rheometers and measurement geometries. Mater Struct ***53****, 92 (2020).* https://doi.org/10.1617/s11527-020-01477-w

Research question:

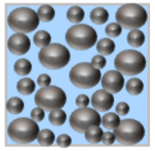
To which extent are Parallel-Plate rheometry and Vane-in-Cup rheometry comparable for pastes with ***increasing non-Newtonian viscosities****?*

Experimental framework – Concept of investigation

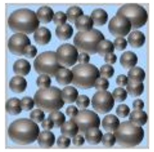


Experimental framework – Mixture proportions

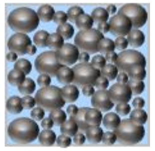
Solid volume fraction ϕ_s



$\phi = 0.45$



$\phi = 0.52$



$\phi = 0.55$

Binders

CEM I 42.5 R

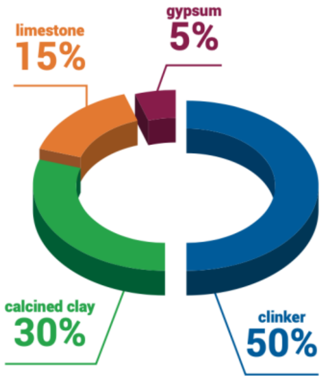
Data in brief https://doi.org/10.1016/j.dib.2019.104699

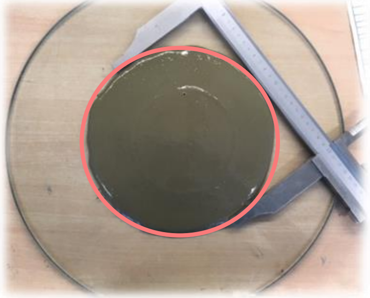
Limestone-calcined-clay compound (LC3)

Data in brief https://doi.org/10.1016/j.dib.2023.108902

Mixtures

Test series	Solid volume fraction ϕ [-]	Water / binder ratio [-]	Cement [kg/m³]	Water [kg/m]	PCE amount [% bwoc]
OPC-0.45	0.45	0.39	1399.5	550.0	0.24
OPC-0.52	0.52	0.30	1617.2	480.0	0.85
OPC-0.55	0.55	0.26	1710.5	450.0	1.40
LC3-0.45	0.45	0.42	1295.1	550.0	0.22
LC3-0.52	0.52	0.32	1496.6	480.0	0.75
LC3-0.55	0.55	0.28	1582.9	450.0	1.07



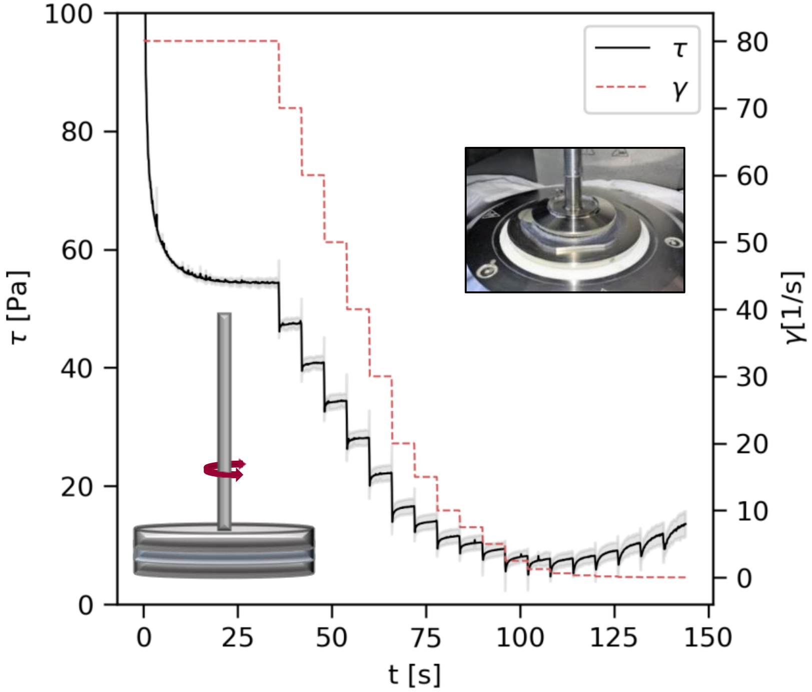


$$\tau_0 = \frac{225\rho g V^2}{128\pi^2 r^5}$$

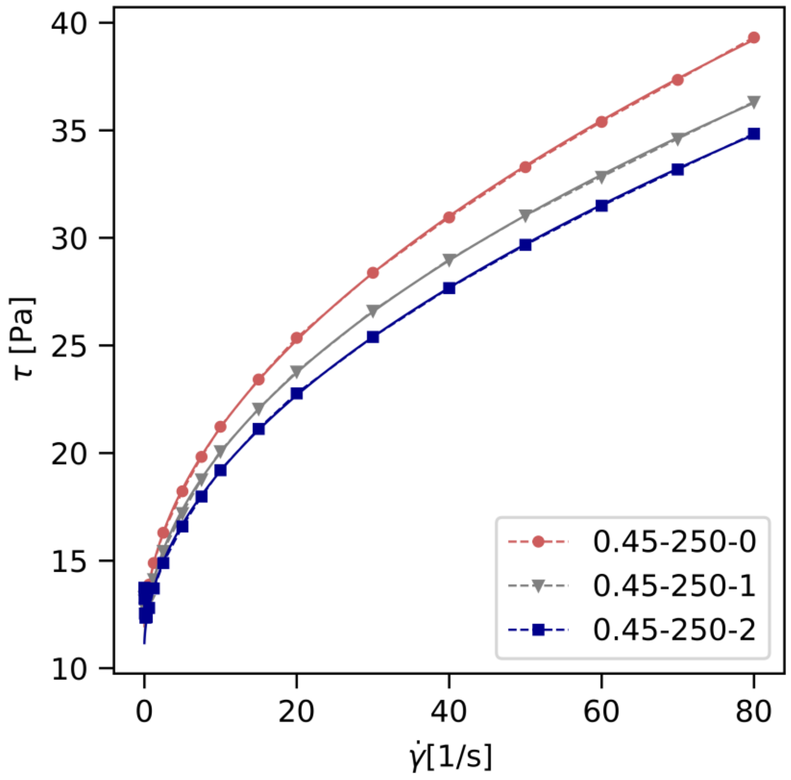
Similar slump flow at t_{final}

Experimental framework – parallel plate measurements

Raw data



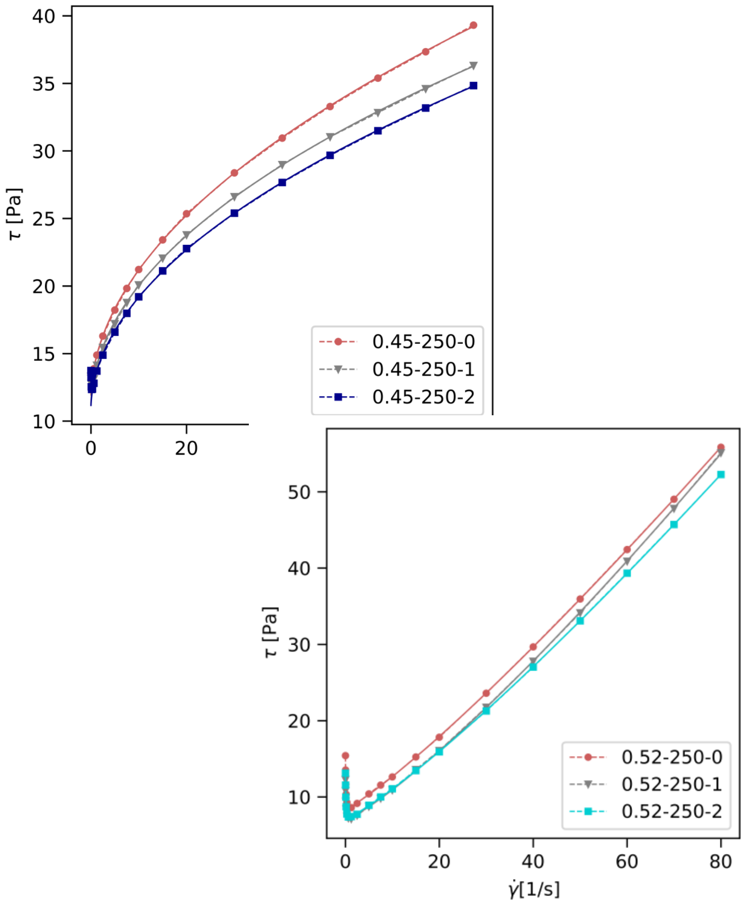
Flow curves



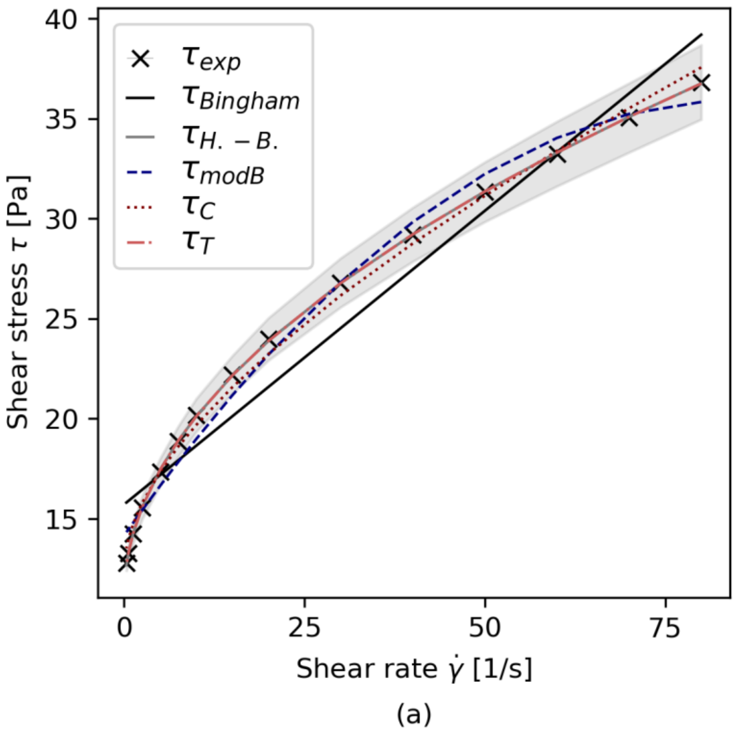
- Step-rate down profile
- Each shear rate step duration of 6 seconds
  - ➢ Required time for reaching an equilibrium
- Analysis of equilibrium stress per step
- Plot of $\dot{\gamma} - \tau$ flow curve

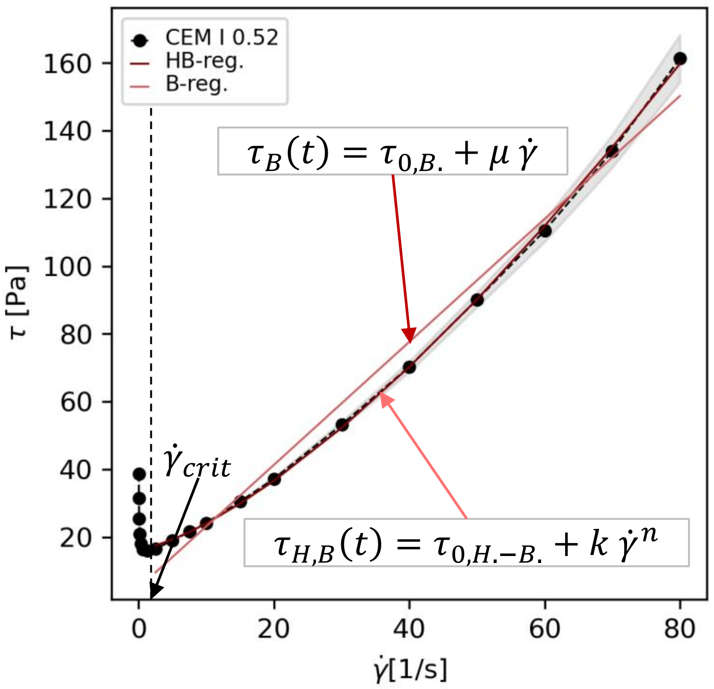
Experimental framework – parallel plate measurements

Flow curves



Phenomenological regression analysis





- General regression analysis with different phenomenological models
  - ➢ Bingham model
  - ➢ Herschel-Bulkley model
  - ➢ Modified Bingham model
  - ➢ Casson model
  - ➢ Toussaint model

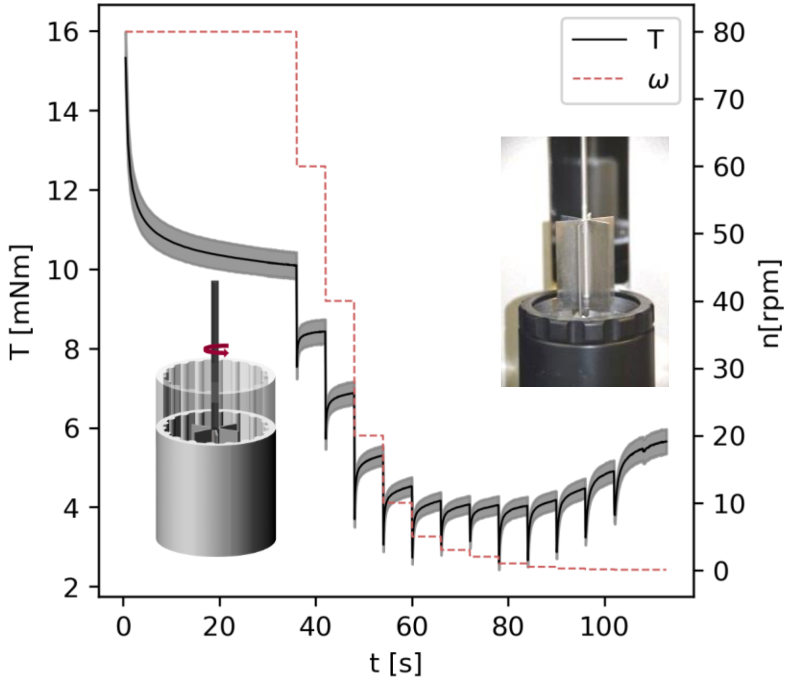
$$\tau = \tau_{0,H.-B.} + k\dot{\gamma}^n \text{ for } \tau > \dot{\gamma}_{\text{crit}}$$

$$\tau = \tau_{0,B.} + \mu\dot{\gamma} \text{ for } \tau > \dot{\gamma}_{\text{crit}}$$

$$\dot{\gamma} = 0 \; for \; \tau \leq \dot{\gamma}_{\text{crit}}$$

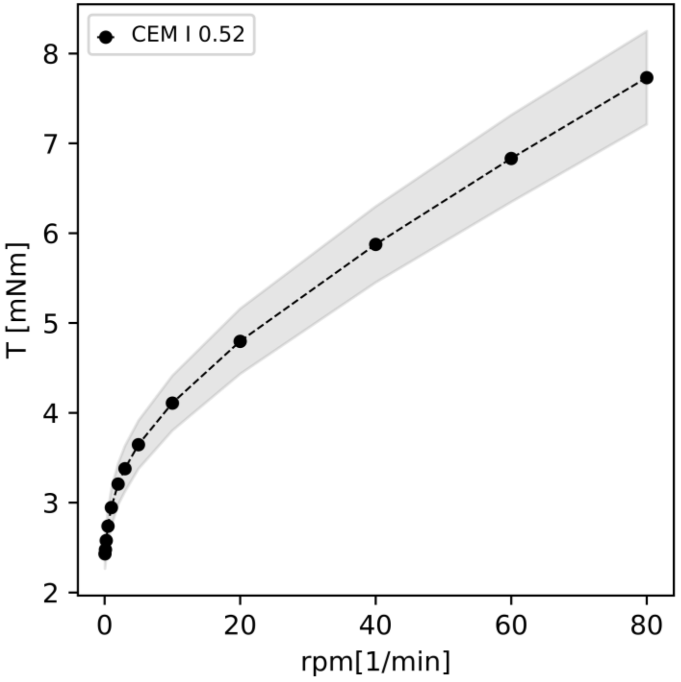
Experimental framework – Vane-in-Cup measurements

Raw data



Raw data analysis

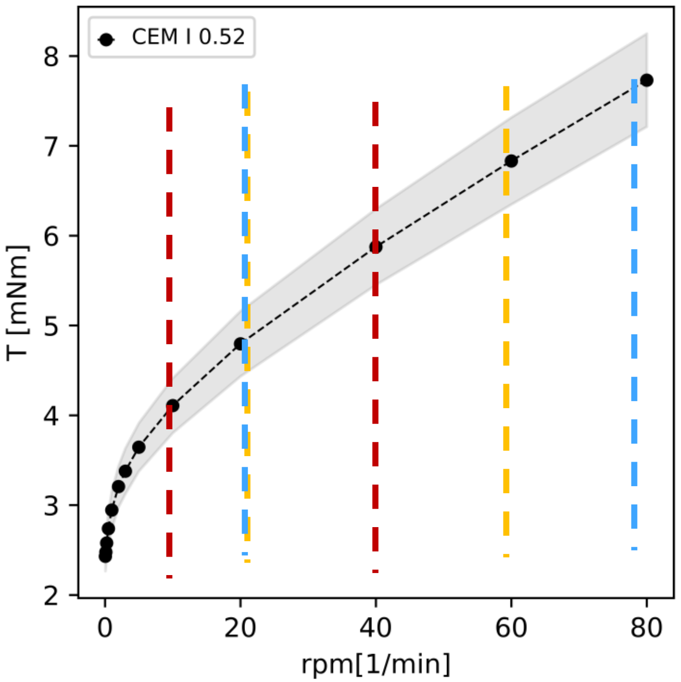
Flow curves



- Step-rate down profile: Definition of rotational speed
- Each rotational speed step duration of 6 seconds
  - ➢ Required time for reaching an equilibrium
- Analysis of equilibrium torque per step
- Plot of $n - T$ flow curve

Experimental framework – Vane-in-Cup measurements

Flow curve



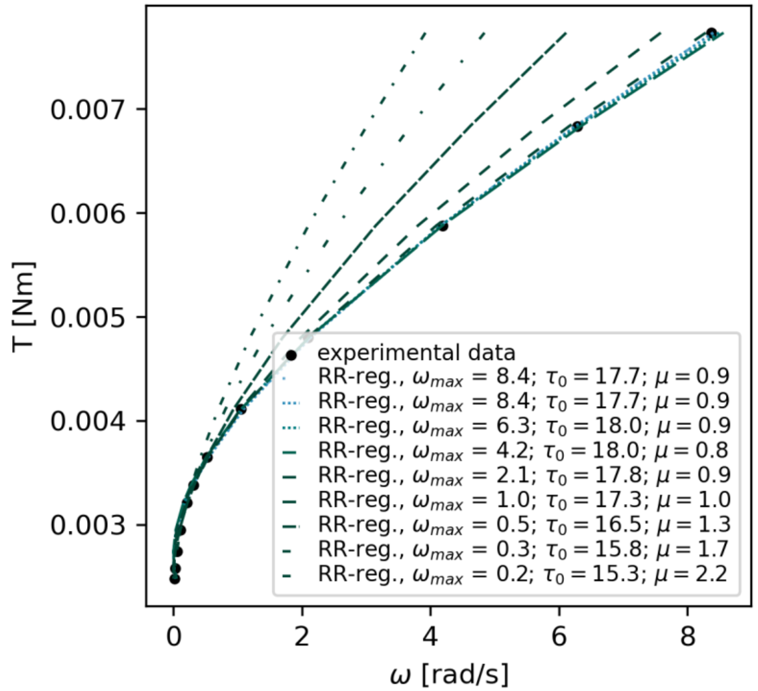
Rheological parameter analysis

$$\omega = \left(\frac{T}{4\pi h \mu}\right)\left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) - \left(\frac{\tau_{0,B}}{\mu}\right)\ln\left(\frac{R_o}{R_i}\right)$$

$$\tau(\dot{\gamma}) = \tau_{0,B} + \mu\,\dot{\gamma}$$

Input range: Definition of ω_{min} and ω_{max}

- Variation of ω_{min} and ω_{max}
- Variation of size of ω array



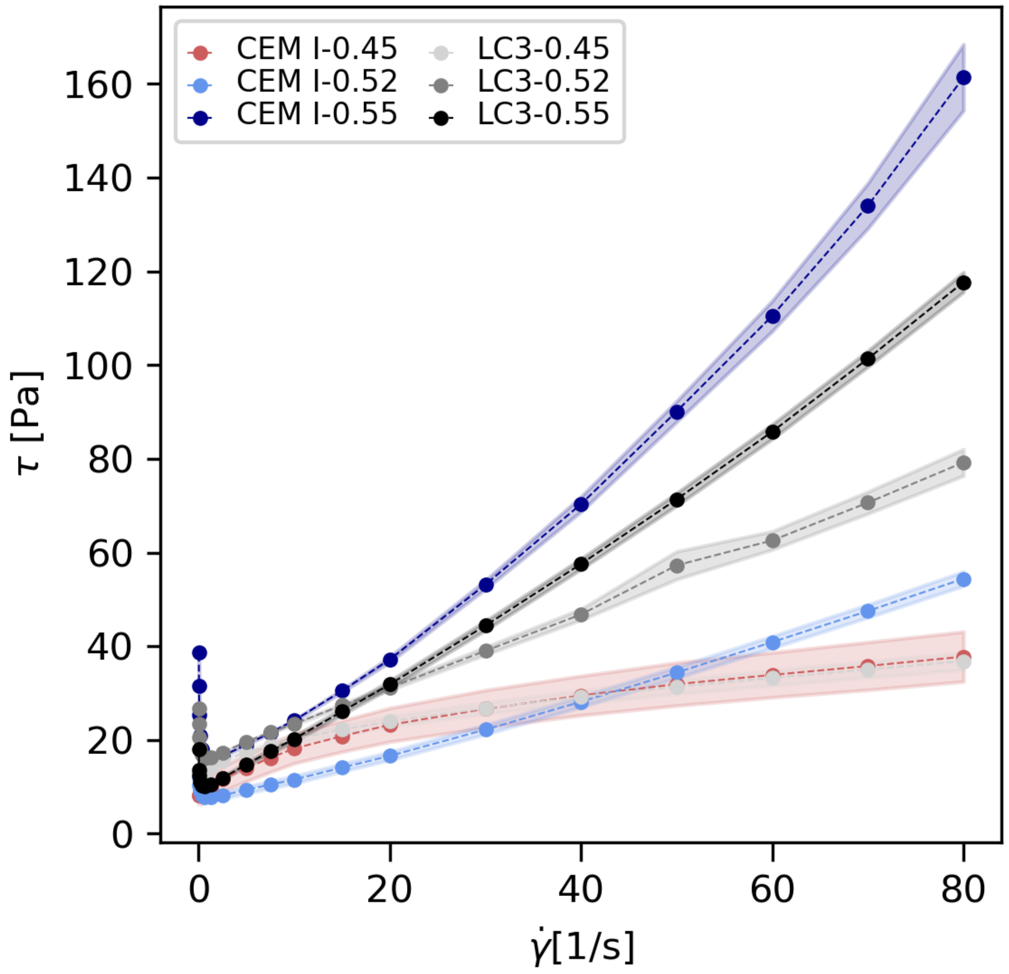
Results – parallel plate measurements

Test series	Critical shear $\dot{\gamma}_{crit}$ [s⁻¹]	Yield stress $\tau_{0,B}$ [Pa]	Plastic viscosity µ $[Pas]$	Yield stress $\tau_{0,B}$ [Pa]	Consistency index k [Pasⁿ]	Non-Newtonian index [-]
OPC-0.45	0.02	11.13	0.38	6.53	3.69	0.49
OPC-0.52	1.25	5.53	0.59	7.53	0.26	1.18
OPC-0.55	1.25	5.00	1.82	16.45	0.29	1.41
LC3-0.45	0.16	15.71	0.29	11.05	2.86	0.50
LC3-0.52	0.63	15.47	0.80	15.35	0.82	0.99
LC3-0.55	0.63	6.79	1.34	10.50	0.63	1.17

**Bingham and Herschel-Bulkley analysis solely for flow beyond critical shear rate $\dot{\gamma}_{crit}$*

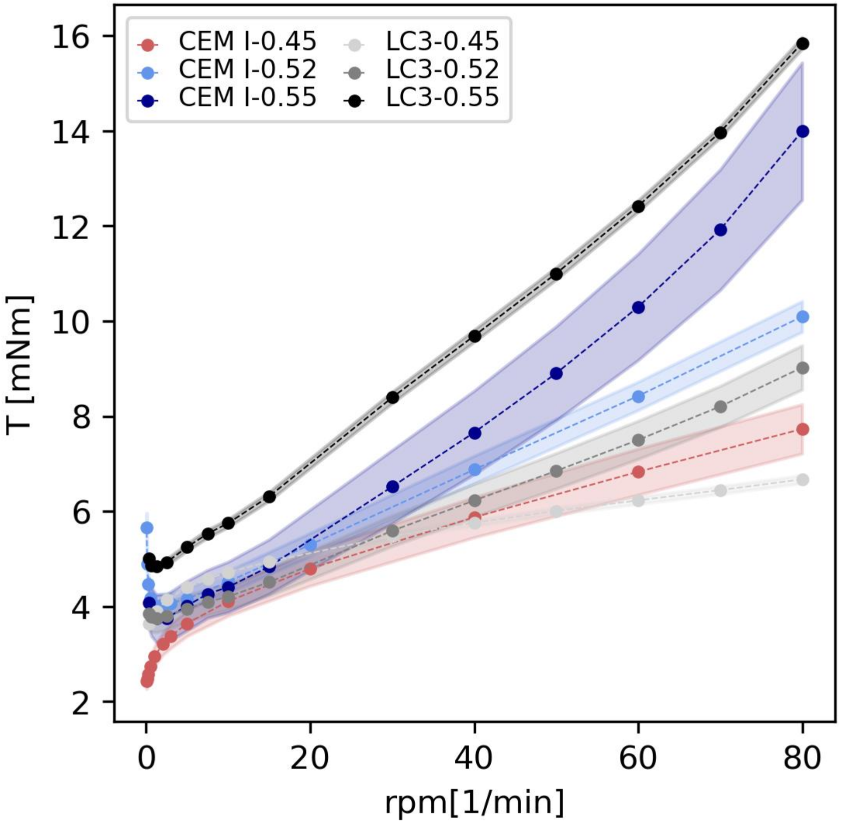
- Larger effect of Φ_s on CEM I paste rheology than on LC3 pastes
- Paste rheology ranges from shear-thinning to shear-thickening
- Table shows parameter analysis for Bingham and Herschel-Bulkley parameters – yield stress variation highest at highest Φ_s

Flow curves



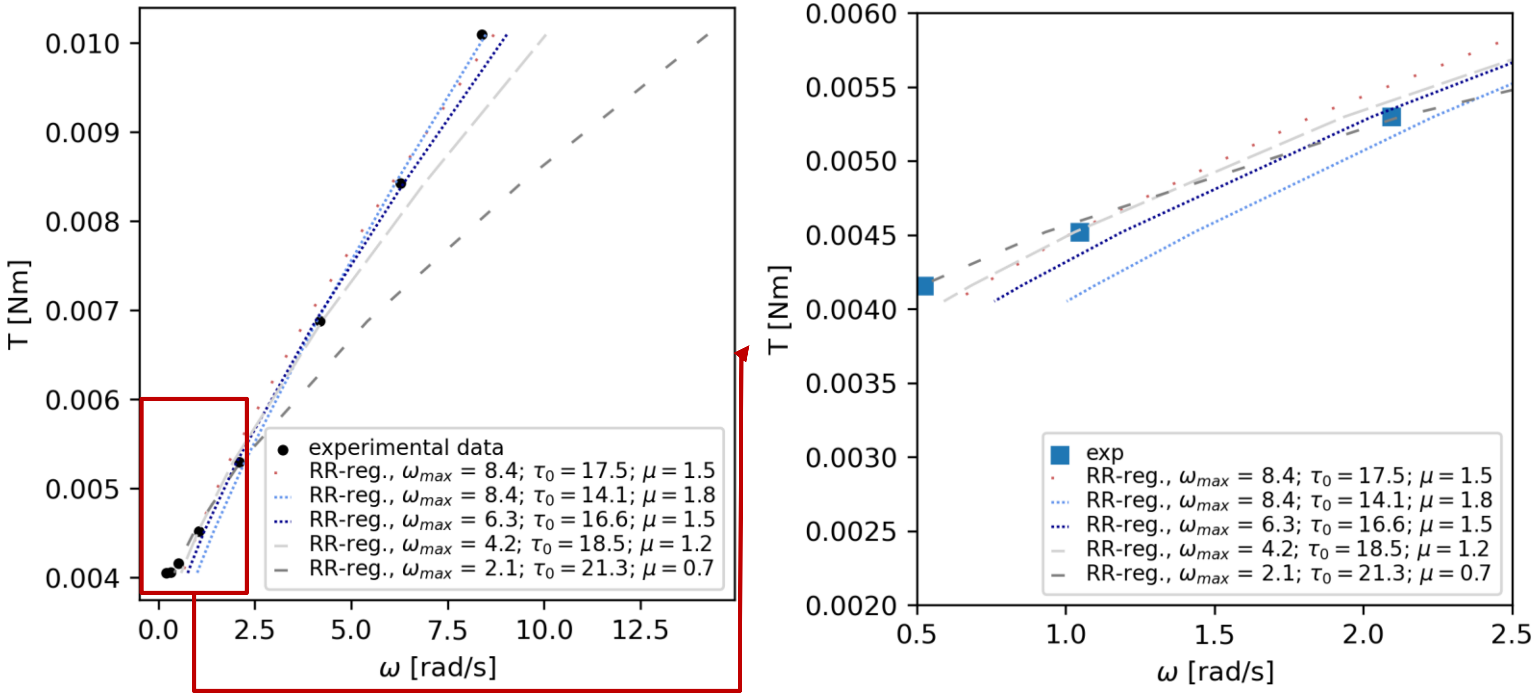
Results – Vane-in-Cup measurements

Flow curves



- Standard variation within test series higher for CEM I pastes
- Pastes show shear-thinning to shear-thickening behavior as well

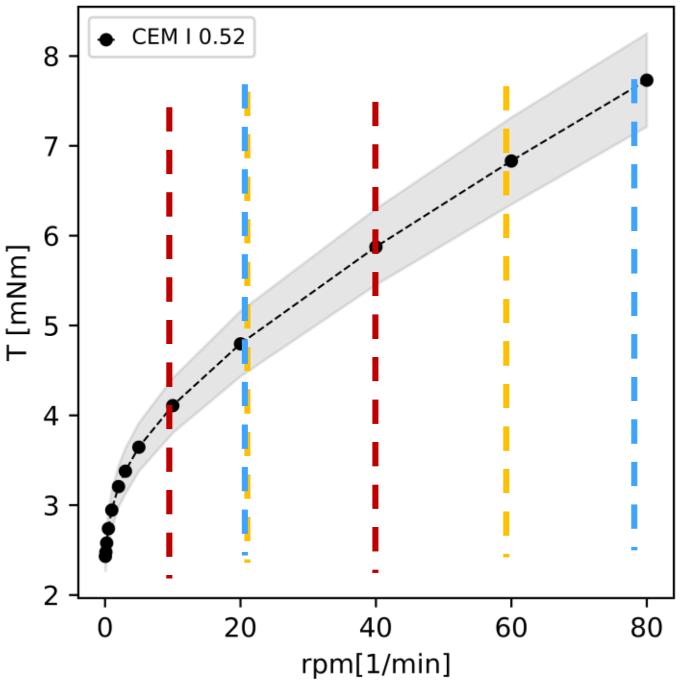
Application of Reiner-Riwlin equation



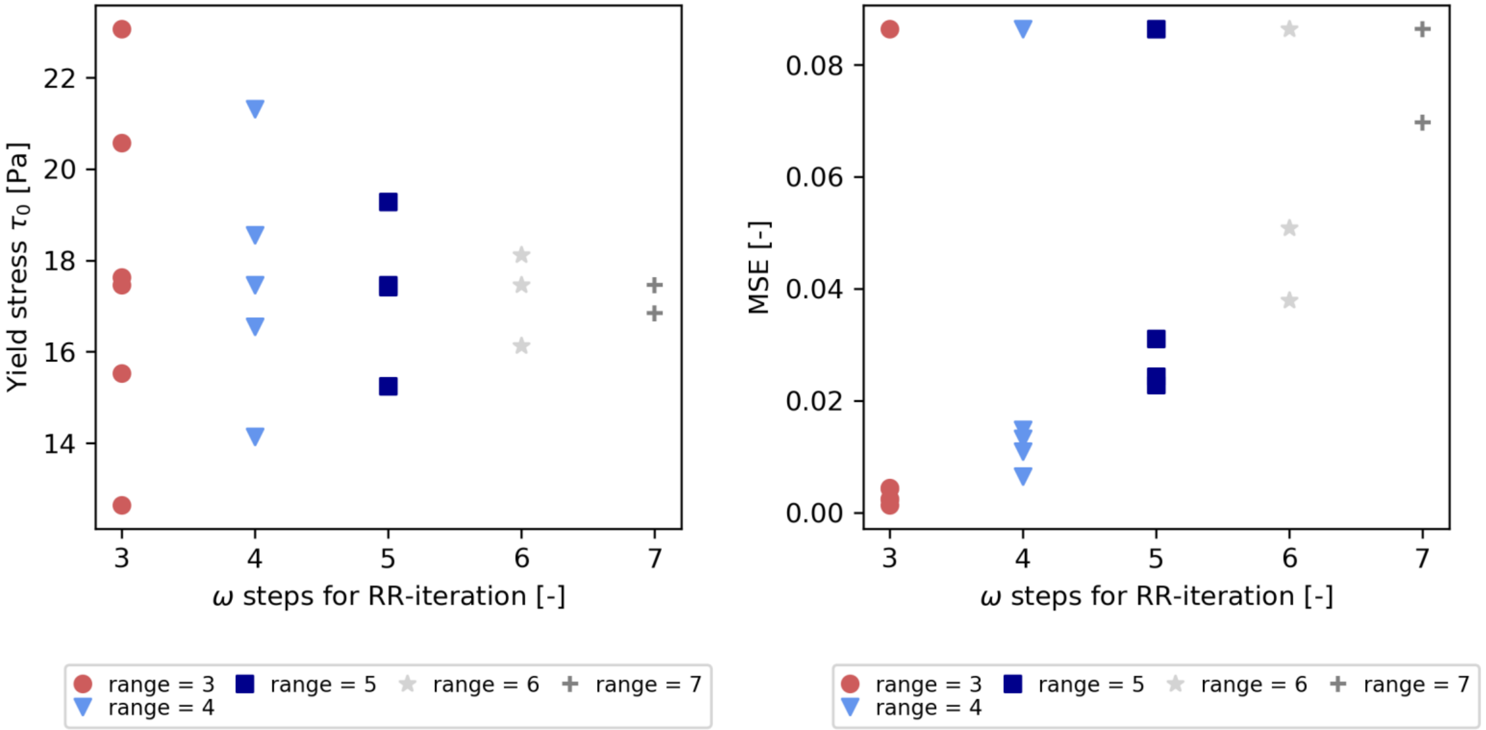
- Loopwise application of RR-equation for different $\omega_{min} - \omega_{max}$ - input ranges
- Fit curves that fit well at high ω – values do not fit in the range of low ω
- Number of possible RR-loops depends on the size of ω-array as input

Results – Vane-in-Cup measurements

Remember

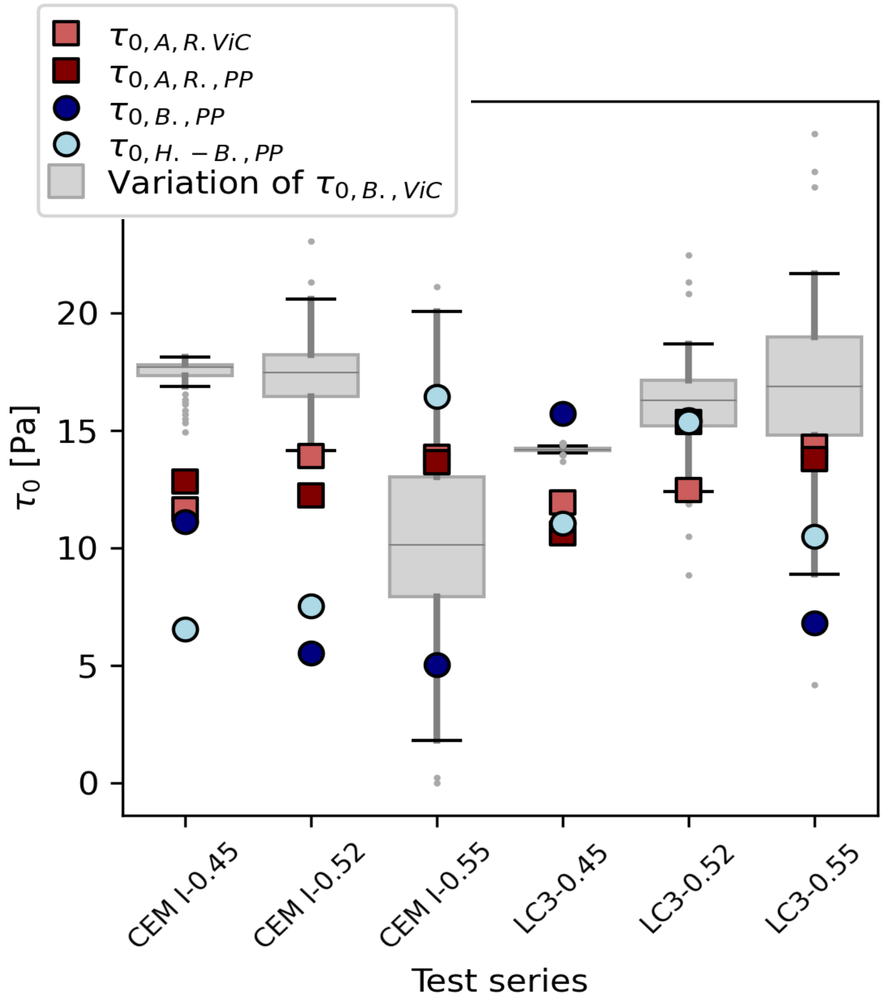


Variation of yield stress values



- With increasing size of ω-array as input, calculated $\tau_{0,ViC}$ yields towards a mean value
- This goes along with the highest mean squared error for the fitting function
- At low size of ω-array, highest variations of calculated values occur, along with the highest and lowest MSE

Results – Yield stress comparison



- Strong dependency of the calculated yield stress on the chosen
  - rheometric device
  - regression method
  - input data range
- With increasing non-Newtonian index n, the choice of raw data handling and rheological parameter calculation becomes crucial
- The choice of ω_{min} and ω_{max} can under- or overestimate the "real" yield stress
- Since the Reiner-Riwlin equation calculates a linear, plastic viscosity μ and a Bingham yield stress $\tau_{0,B}$, its application with increasing n becomes questionable

Concluding remarks & Outlook

- While the parallel plate device enables direct calculation of rheological data, it cannot measure materials with larger particle sizes
- However, the Vane-in-Cup rheometer requires the calculation of rheological data by a fitting function that is based on Bingham material behavior

➢ Other models should be integrated into the Reiner-Riwlin equation to account for non-Newtonian viscosities
  - Next step: Implementation of the modified Bingham model as proposed by Feys, D. et al.:

Feys, D., Wallevik, J.E., Yahia, A. et al. Extension of the Reiner–Riwlin equation to determine modified Bingham parameters measured in coaxial cylinders rheometers. Mater Struct ***46****, 289–311 (2013). https://doi.org/10.1617/s11527-012-9902-6*

Preprint article with rheological data available here:

https://doi.org/10.20944/preprints202402.0703.v1

Thank you very much! I am open for discussions and questions!

Rheometric raw data for own mathematical analysis and python code available soon open-source or upon request