Structure-effect relationship between modern superplasticizers and the rheological properties of fresh cement pastes

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25. Kolloquium
Rheologische Messungen an mineralischen Baustoffen
2.+3. März 2016
OTH Regensburg
Motivation

Typical problems observed in practice

- Incompatibilities between cement and superplasticizers (SP) lead to insufficient rheological properties.
- No systematic correlation between SP-structure, cement properties and rheological behaviour of paste known.
- Empiricism in the mix design process ("Trial and Error").
- Damages on concrete structures may occur.

Scattering properties due to cement-superplasticizer incompatibilities

![Graph showing Haagermann spread flow (mm) vs investigated batch (mm)]

- Cement paste at w/c = 0.43 with 0.3% SP
Goal of the project

Modelling of effect of SP dosage on rheology

1. Understanding the particle-particle and particle-fluid interaction with and without the presence of superplasticizers

2. Quantification of the influence of superplasticizers on the rheological properties of fresh cement pastes

3. Modelling the rheological properties of fresh cement suspensions with and w/o SP as a function of the physical properties of the raw materials
Flow behaviour of pure cement pastes
Measurement set-up

Combined measurement of

rheological properties

inter-action

zeta-potential and degree of agglomeration of particles
Elastic properties of fresh cement pastes

**Characteristics**
- shear modulus: \( G^* = \tau_A / \gamma_A \)
- viscoelasticity
  - phase shift \( \delta \)

**Conclusions**
- shear deformation characterized by:
  - elastic material response with const. shear modulus for low shear stresses
  - structural breakdown when critical stress level is exceeded

**Diagram**
- Shear stress vs. shear deformation
- Elastic range, breakdown, viscous range
- Critical shear stress level = structural limit stress \( \tau_s \)
- Critical shear stress level = \( \tau_A \)
Creep deformation at subcritical shear stresses

Viscous flow at low shear loadings

shear loading \( \tau_c = 5 \text{ Pa} \) \( \tau_c = 0 \text{ Pa} \)

Viscous flow at high shear loadings

\[ \eta_c = \frac{\tau}{\dot{\gamma}_{c,\infty}} \]

Information on physical origins of rheological behaviour missing

\[ \eta = \frac{\tau}{\dot{\gamma}} \]
Measurement of particle interactions

Measurement principle

- Pressure sensor
- Carrier liquid
- Cement-particle
- Electrode
- Ultrasound
- Electric field
- Particles
- Pressure amplitude
- \( \zeta \)-potential

Measurement result

- In-situ agglomerate size

Further reading:

Debye, P.: A method for the determination of the mass of electrolythic ions. In: Journal of Chemical Physics 1 (1933), pp. 13-16


Rheological modelling

Base elements

- spring
- dash-pot
- friction element

Parameters defined as functions of:
- Blaine value
- mean particle size
- particle mineralogy
- phase content $\phi$
- packing density $\phi_p$

**elastic**

**creep**

**flow**
Rheology of superplasticizer-modified pastes
# State of knowledge

## Literature review regarding cement – superplasticizer interaction: qualitative results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Yield stress $\tau_0$</th>
<th>Viscosity $\mu$</th>
<th>SP-adsorption</th>
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<tr>
<td>C$_3$A / C$_4$AF-content</td>
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<tr>
<td>Sulfate content</td>
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<tr>
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<tr>
<td>Molecular weight</td>
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**Legend:**
- **increasing** $\uparrow$
- **decreasing** $\downarrow$
- **influence not clear** $\rightarrow$

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March 2\textsuperscript{nd}, 2016

Structure-effect relationship for superplasticizer efficiency

Raphael Breiner, Michael Haist and Harald S. Müller
Experimental programme

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<tr>
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<td>D</td>
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</table>

**sum (for a single dosage)** 121

**PCE Superplasticizers (examples):**
- **charge density**
  - PCE A: ![Charge Density](image)
  - PCE B: ![Charge Density](image)
- **side chain length**
  - PCE A: ![Side Chain](image)
  - PCE B: ![Side Chain](image)
  - PCE C: ![Side Chain](image)
Influence of SP-dosage on yield stress

Producer A: CEM I 42.5 R; w/c = 0.4

Producer B: CEM I 42.5 R; w/c = 0.4

Relative yield stress $\frac{\tau_{0,SP}}{\tau_0}$ as a function of SP-dosage [% by mass of cement].

- Producer A: CEM I 42.5 R
  - PCE-A
  - PCE-B
  - PCE-C

- Producer B: CEM I 42.5 R
  - PCE-A
  - PCE-B
  - PCE-C

Influence of SP-dosage on yield stress

Producer A: CEM I 42.5 R; w/c = 0.4

Producer B: CEM I 42.5 R; w/c = 0.4

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- Producer A: CEM I 42.5 R
  - PCE-A
  - PCE-B
  - PCE-C

- Producer B: CEM I 42.5 R
  - PCE-A
  - PCE-B
  - PCE-C
Influence of SP-dosage on yield stress

Producer A: CEM I 42.5 R; w/c = 0.4

Producer B: CEM I 42.5 R; w/c = 0.4

C₃A-content: 6.4 %
sulfate content: 3.7 %
hemihydrate: 1.6 %

C₃A-content: 4.9 %
sulfate content: 4.5 %
hemihydrate: 1.4 %
Influence of SP-dosage on plastic viscosity

Producer A: CEM I 42.5 R; w/c = 0.4

Producer B: CEM I 42.5 R; w/c = 0.4
Influence of SP-dosage on plastic viscosity

Producer A: CEM I 42.5 R; w/c = 0.4

Producer B: CEM I 42.5 R; w/c = 0.4

- **C₃A-content**: 6.4%
- **sulfate content**: 3.7%
- **hemihydrate**: 1.6%

- **C₃A-content**: 4.9%
- **sulfate content**: 4.5%
- **hemihydrate**: 1.4%
Influence of sulfate agent

Producer A: clinker powder CEM I 42.5 R; iron sulfate 0.5 %

Conclusions
- Properties depending on the composition of the sulfate agent
- Increasing part of hemihydrate (H) improves workability
Adsorption behaviour of SP
Adsorption of superplasticizer

Cement CEM I 42.5 R; w/c = 0.4; extraction of filtrate 15 min after water addition

- Size exclusion chromatography (SEC)
- Separation columns with porous gel (defined pore size)

Small molecules move through the gel
Bigger molecules through the channels in between

Graph showing the superplasticizer adsorption [%] vs. molar mass [mol/g] for different superplasticizer types and producers.
Determination of surface interactions

Atomic-Force-Microscopy (AFM) – Setup and expected results

Results

- Preliminary experiments successful
- Both polymers increase the surface interactions
- as expected PCE D shows higher repulsion forces
- Sample preparation procedure suitable

Preliminary experiments successful
Both polymers increase the surface interactions
as expected PCE D shows higher repulsion forces
Sample preparation procedure suitable
Rheological modelling

Base elements

- spring
- dash-pot
- friction element

Parameters defined as functions of:
- Blaine value
- mean particle size
- particle mineralogy
- phase content
- packing density

\[ G_1 \quad \eta_2 \quad \tau_0 \quad \mu \]
Rheological modelling

Base elements

- **spring**
- **dash-pot**
- **friction element**

**Model parameters are modified by SP action**

- Consideration of superplasticizer adsorption
- Consideration of sterical interactions
Modelling of superplasticizer interaction

Example of yield stress calculation for $t = 15$ min.

$$\tau_0 = 391 \times \exp \left\{ \frac{3158 \times \Gamma_0}{\Gamma_{C_3S}} \times \frac{\phi}{\phi_p} \right\} \times f \left( c_{C_3A}; c_{C_4AF}; A; c_S; S \right) \times f \left( c_{SP}, m_{ads}, M_W \right)$$

with

$$\Gamma_{C_3S} = \phi \times \rho_p \times C_{C_3S} \times \Omega_{Blaine}$$

- phase content
- particle density
- Blaine value
- $C_3S$ content

Cement paste model by Haist, 2009

SP adsorption

- $(C_3A, C_4AF$-content, alkalinity, sulfate content, sulfate agent)

Steric hindrance

- (SP dosage, mass of adsorbed polymers, molecular weight)

Structure-effect relationship for superplasticizer efficiency
Model validation

Example of yield stress for t = 15 min.

Conclusions

- Model accounts very well for the underlying interactions
- Careful assessment necessary, as some important parameters still kept constant
- Too limited to be generally accepted at the moment

\[ \Gamma_{C_3S} ; c_{C_3A} ; c_{C_4AF} ; c_S ; S ; A \]

- Input of cement properties
- Input of SP properties
- \( w/c = 0.4 \)
- \( t = 15 \text{ min.} \)
Thank you very much for your attention

The financing by the Helmholtz Association and the support by OPTERRA and BASF are gratefully acknowledged by the authors.
Behaviour at small shear loadings

**Producer A: CEM I 42.5 R; t = 15 min.**

- Rheological behaviour differs clearly
- Elastic properties of the suspension survive despite a SP-addition

**Producer B: CEM I 42.5 R; t = 15 min.**

Conclusions

- Rheological behaviour differs clearly
- Elastic properties of the suspension survive despite a SP-addition
Current investigations AFM

So far: Measurement SiO$_2$ – cement clinker

- Measuring tip
- Superplasticizer solution
- Cement clinker in epoxy resin

Now: Measurement cement grain on cement grain

- Measuring tip
- (cement grain)
- Superplasticizer solution
- Cement grain on silicon-wafer
Determination of surface interactions (1)

Atomic-Force-Microscopy (AFM) – principle

- "Raster-Kraft-Mikroskopie"
- Bending of a tip (cantilever) depending on the position as a measure for surface forces
- Force-distance-curves to describe the superplasticizer interactions
Determination of adsorption behaviour

**Size exclusion chromatography (SEC)**

- "Gel-Permeations-Chromatographie" (GPC)
- Separation column with porous gel (defined pore size)
- Small molecules move through the gel
- Bigger molecules through the channels in between

![Diagram](image)

**Comparison with calibration standard**

- Conversion with calibration standard
- Comparison with reference

**Graphs**

- Detector signal [mV] vs. eluation time [min.]
  - PCE X
  - PCE Y

- Polymer-adsorption [%] vs. molecular weight [g/mol]
  - PCE X
  - PCE Y
Modelling for pure cement pastes

Limitation of current model

- Interaction effects from the growth of hydrate phases cannot be considered
- Consideration of steric hindrance from superplasticizers by limitation to the DLVO-theory not possible

Prediction of Zeta potential based on raw material characteristics
- fineness
- density
- mineralogy
- others

Modelling for pure cement pastes

![Diagram](image-url)
Creep deformation at subcritical shear stresses

- Creep deformation at subcritical shear stresses
  - $\tau_c = 5$ Pa
  - $\tau_c = 0$ Pa
  - Creep velocity $\dot{\gamma}_{c,\infty}$
  - Creep deformation
  - Re-creep deformation
  - Elastic deformation
Flow behaviour of fresh cement pastes

Flow behaviour

Conclusions

- Viscous behavior at low shear rates
- Pronounced loss in dynamic viscosity for increasing shear rate

Bingham Modell

\[ \tau(\dot{\gamma}) = \tau_0 + \mu \cdot \dot{\gamma} \]
Modelling of superplasticizer interaction

Example of yield stress calculation for $t = 15$ min.

$$
\tau_0 = 391 \times \exp \left\{ \frac{3158 \times \Gamma_0}{\Gamma_{C_3S} \times \phi_p} \right\} \times f\left( c_{C_3A}, c_{C_4AF}, A, c_S, S \right) \times f\left( c_{SP}, m_{ads}, M_W \right)
$$

with $\Gamma_{C_3S} = \phi \times \rho_p \times c_{C_3S} \times \text{Blaine}$

- Consideration of superplasticizer adsorption
  (C$_3$A-content $c_{C3A}$, C$_4$AF-content $c_{C4AF}$, alkalinity, sulfate content $c_S$, sulfate agent)

- Consideration of sterical interactions
  (SP dosage, mass of adsorbed polymers, molecular weight)

Structure-effect relationship for superplasticizer efficiency