Eine einfache experimentelle Methode zur qualitativen Bewertung des Einflusses beliebiger Polycarboxylatether-Fließmittel auf die Rheologie

A rapid experimental method to qualitatively assess the influence of arbitrary polycarboxylate ether superplasticizers on the rheology

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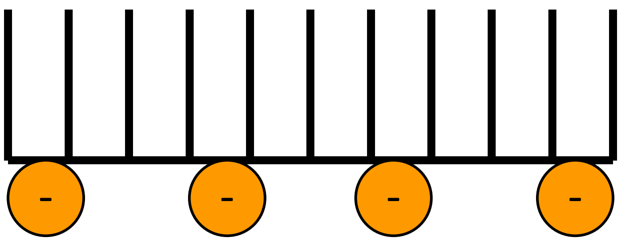
"Rheologische Messungen an mineralischen Baustoffen"
22. Kolloquium und Workshop, Regensburg 2013

The importance of the charge density of PCEs

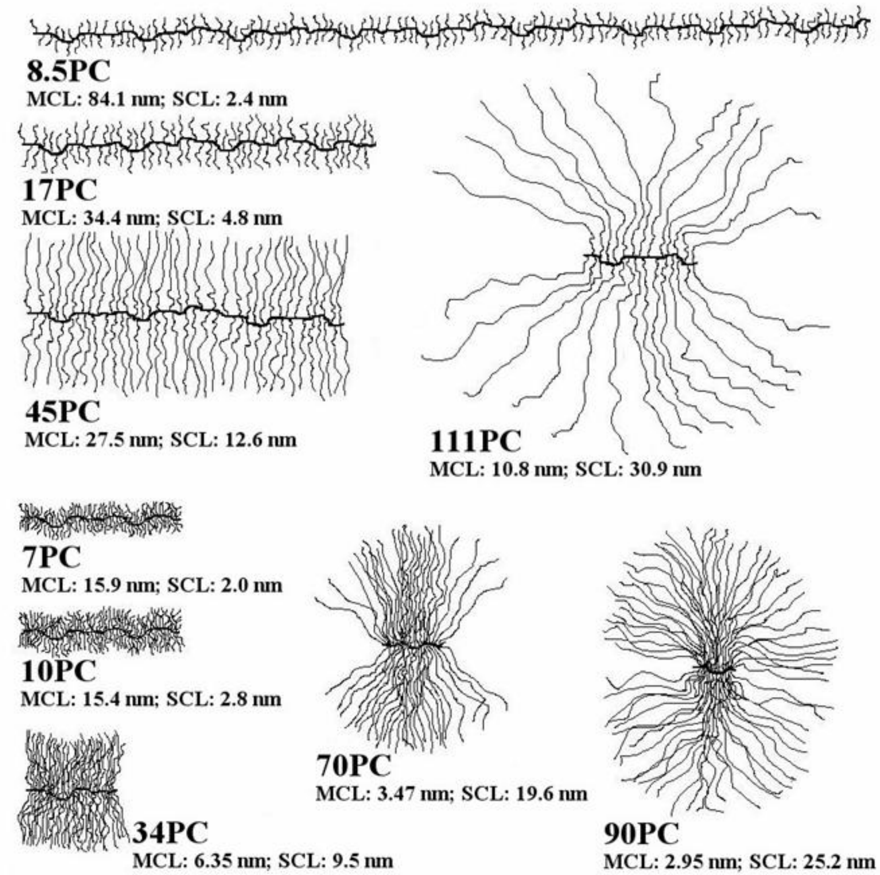
Importance of the charge density of PCE

Polycarboxylic superplasticizers

PEO graft chains



Backbone for adsorption

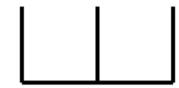
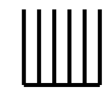


Plank et al., 2006

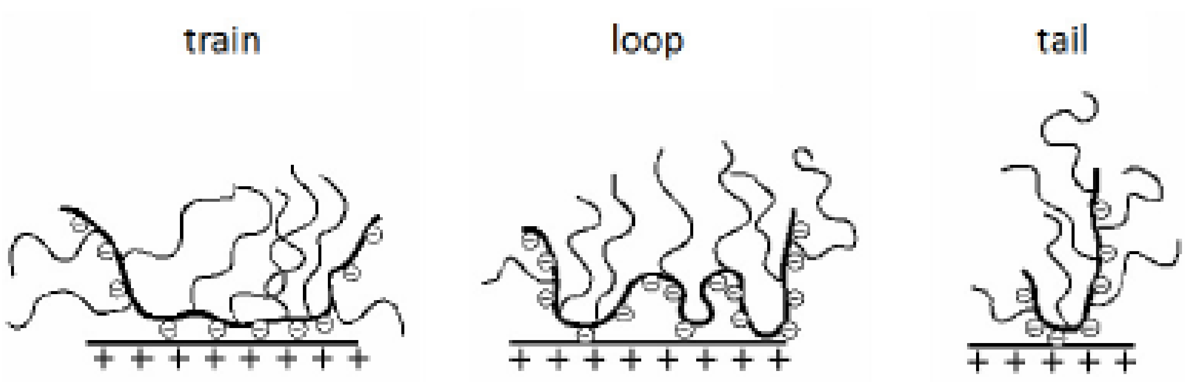
The geometry can be arranged according to requirements.

Importance of the charge density of PCE

Influence of polymeric geometry of PCEs

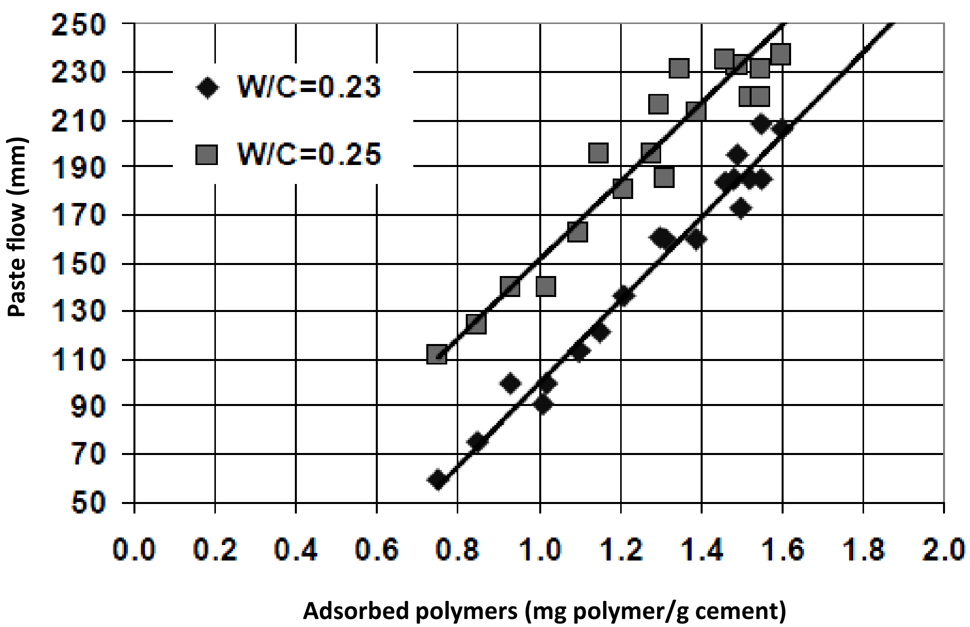
	Relative chain length of trunk polymer	Relative graft length	Relative number of grafts	
Low dispersibility + short dispersibility retention	Long	Short	Large	
High dispersibility	Short	Long	Small	
Long dispersibility retention	Shorter	Long	Large	

After Ohta et al., 1997



Plank et al., 2006

Influence of polymeric geometry of PCEs



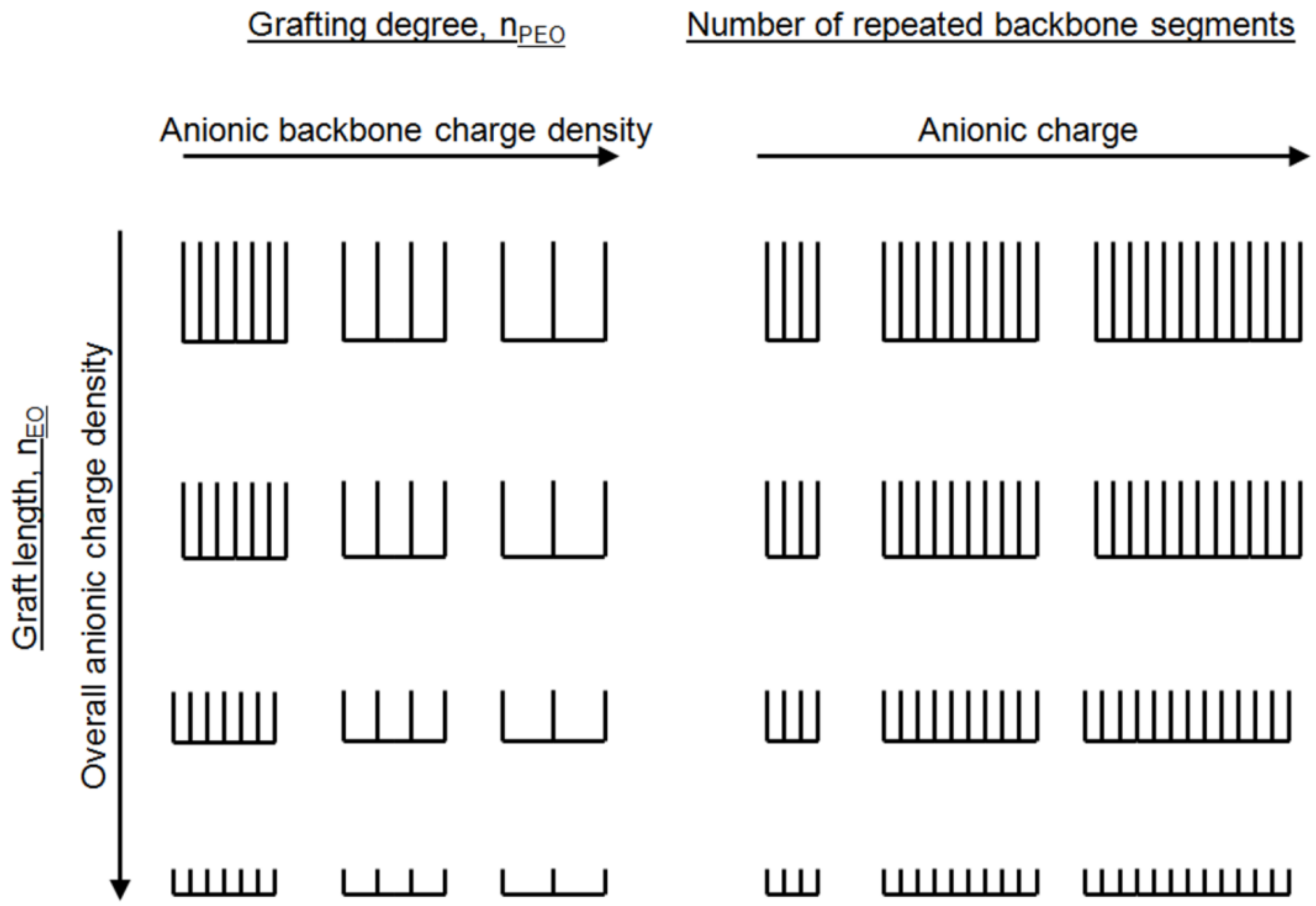
Schober, Flatt et al., 2006

Regardless of the polymeric architecture, the resulting flow spread diameter depends on the amount of adsorbed polymers.

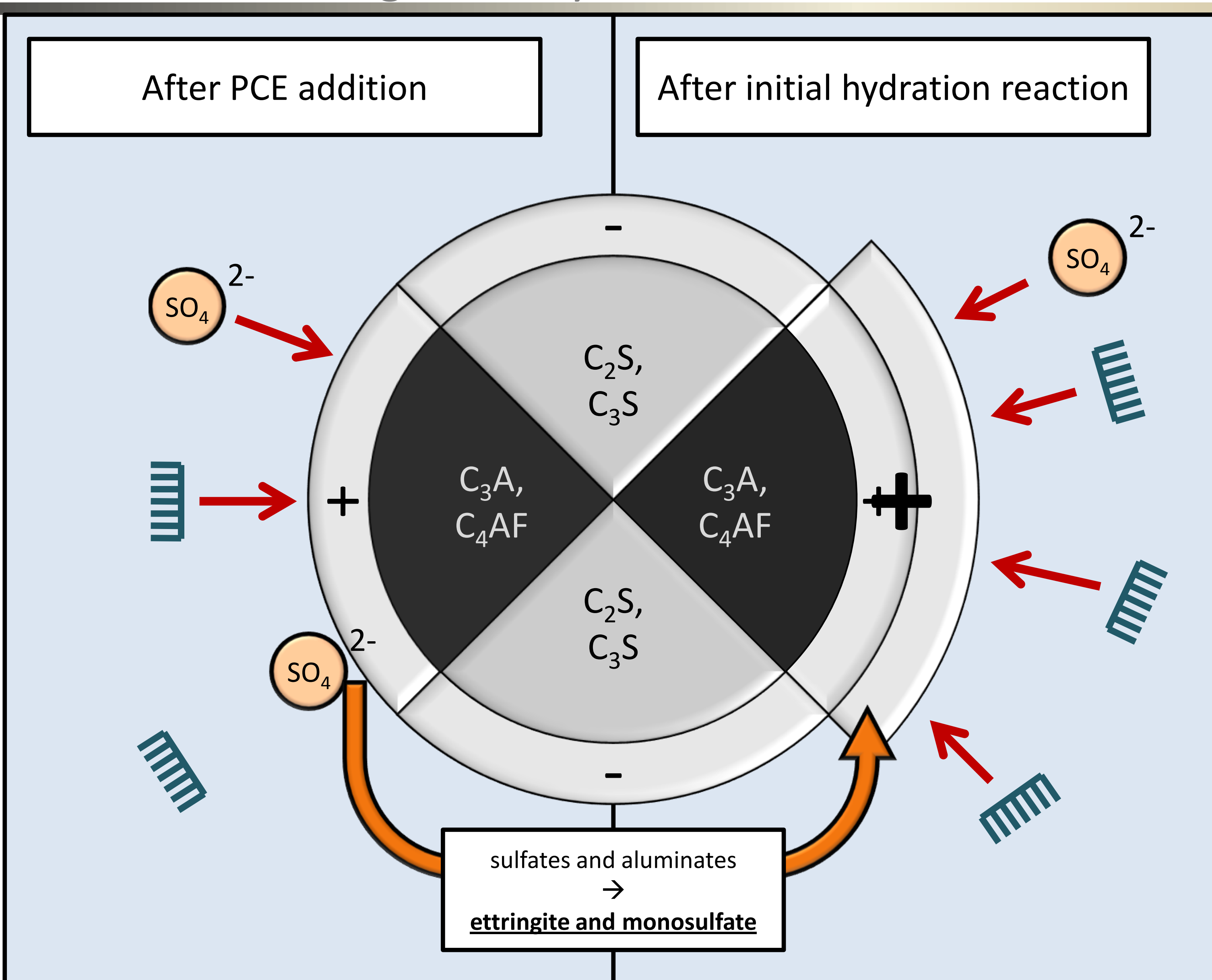
Adsorption of polymers depends on their charges/charge densities.

The influence of the polymeric architecture can be largely limited to its influence on the charge density

Influence of polymeric geometry of PCEs



Importance of the charge density of PCE



How does the charge density affect the rheology?

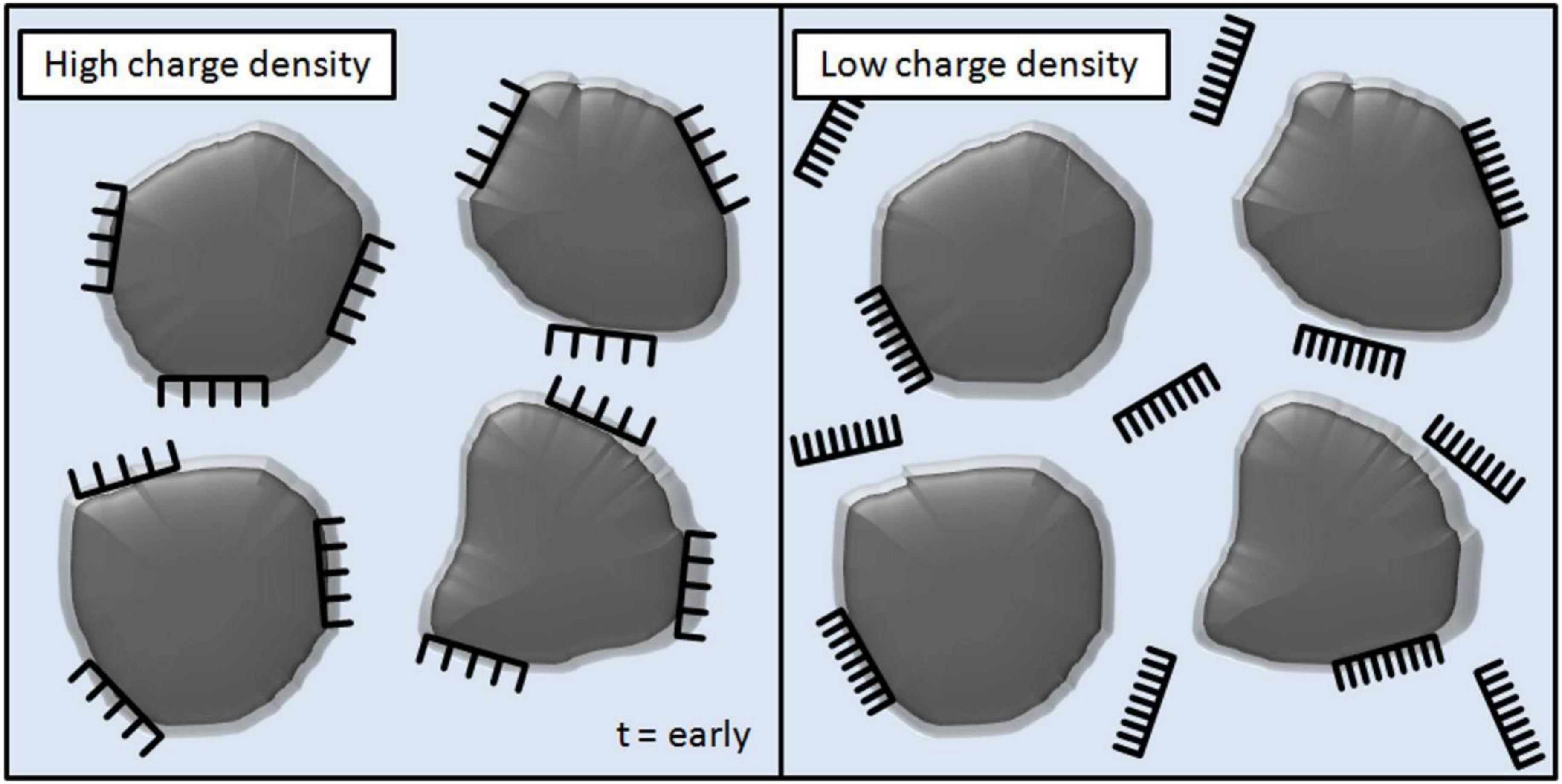
High charge density:

- Rapid adsorption
- Ultimate yield stress reduction

Low charge density:

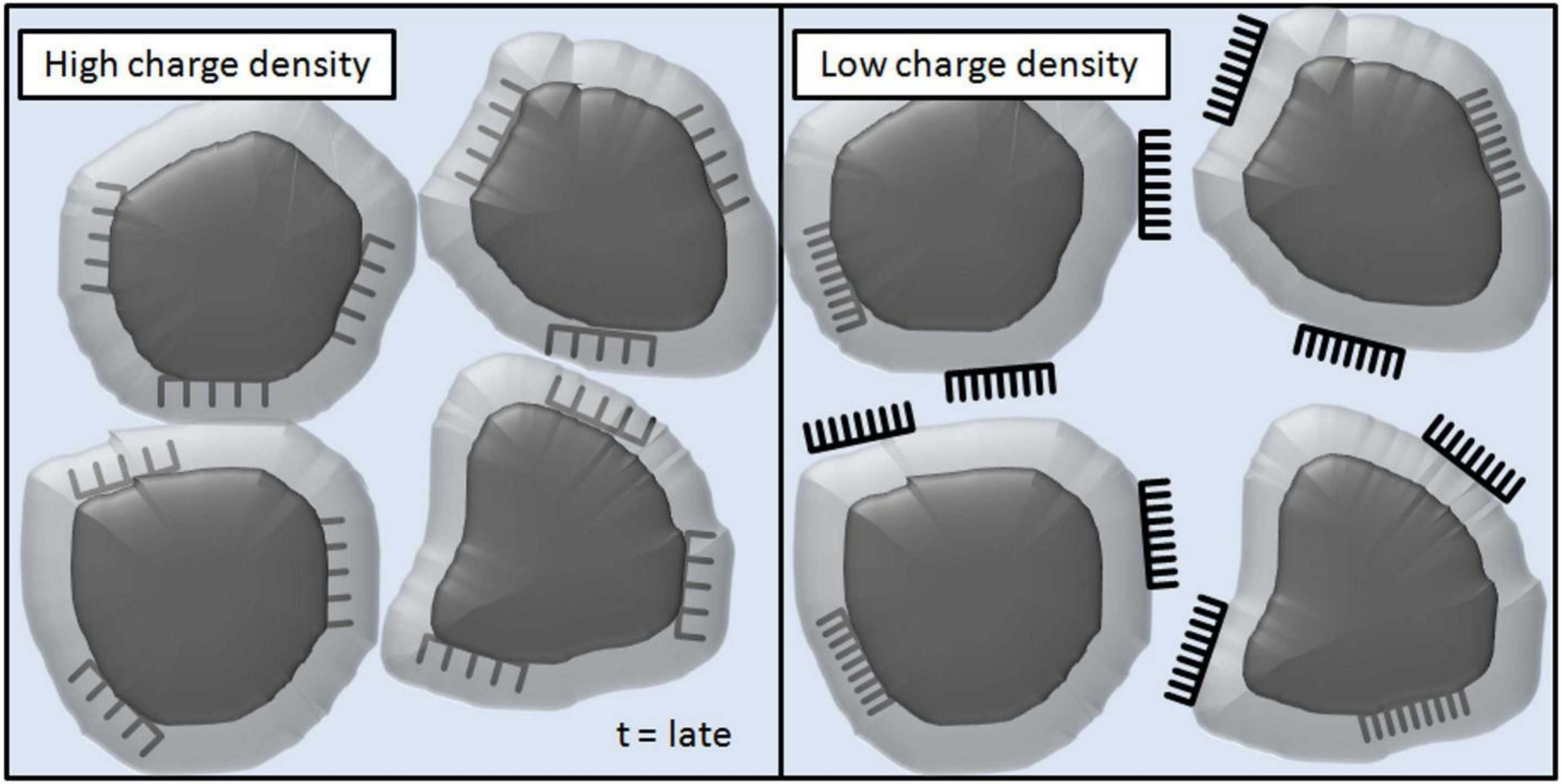
- Slow adsorption
- Average yield stress reduction

How does the charge density affect the rheology?



Rapid adsorption also means rapid consumption upon ongoing hydration.

How does the charge density affect the rheology?



Rapid adsorption also means rapid consumption upon ongoing hydration.

Initially non-adsorbed polymers can adsorb with time.

How does the charge density affect the rheology?

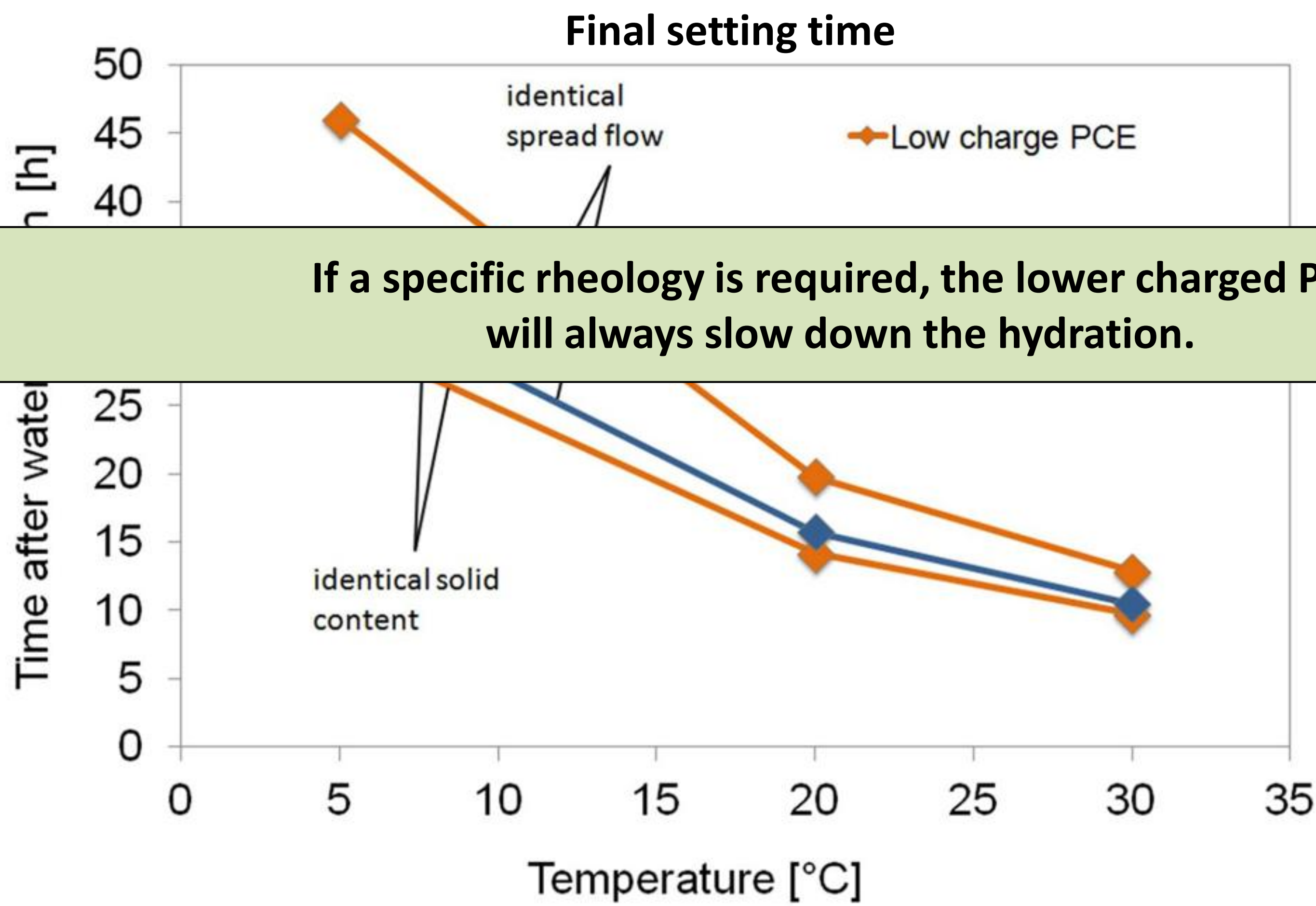
High charge density:

• Rapid adsorption • Ultimate yield stress reduction	• Short performance retention • Segregation risk

Low charge density:

• Slow adsorption • Average yield stress reduction	• Long performance retention • Higher robustness

Effect of PCE charge density on early hydration



If a specific rheology is required, the lower charged PCE will always slow down the hydration.

Effect of PCE charge density on early hydration

High charge density:

• Rapid adsorption • Ultimate yield stress reduction	• Short performance retention • Segregation risk
• Less pronounced retarding effect	

Low charge density:

• Slow adsorption • Average yield stress reduction	• Long performance retention • Higher robustness
• More pronounced retarding effect	

Summary of the influence of the charge density

High charge density:	**Low charge density:**
Ultimate flowability	Good flowability
Short flow retention	Long flow retention
Early setting	Retarded setting

Pre-cast application	**Ready mix application**

Blending is possible.

Two PCEs that distinguish significantly are sufficient
to meet nearly all performance specifications!

How to determine properties without sophistocated methods?

An easy method to distinguish PCE types

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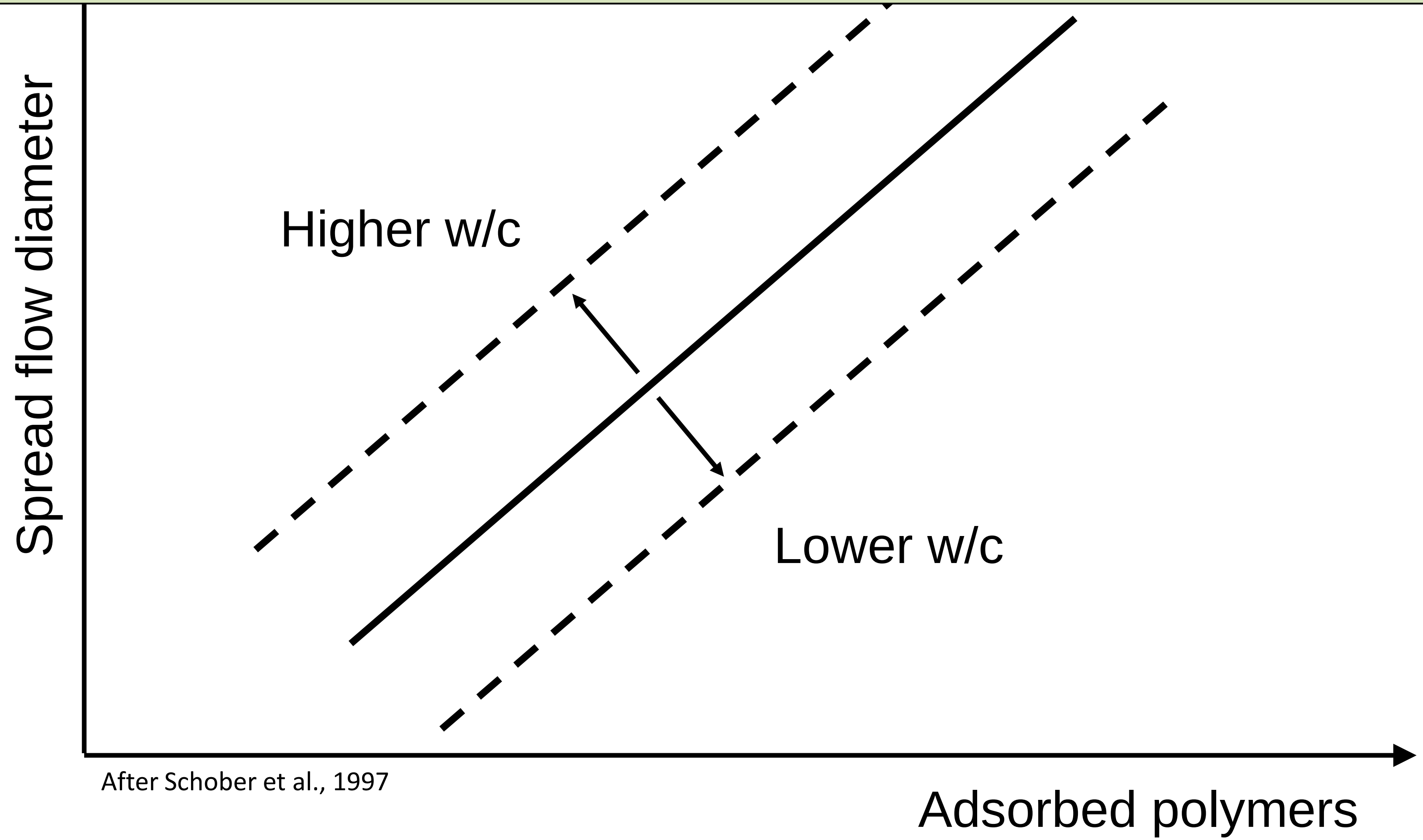
Principle of the test method

Boundary framework

Spread flow correlates in a linear way with the adsorbed polymers at constant w/c.

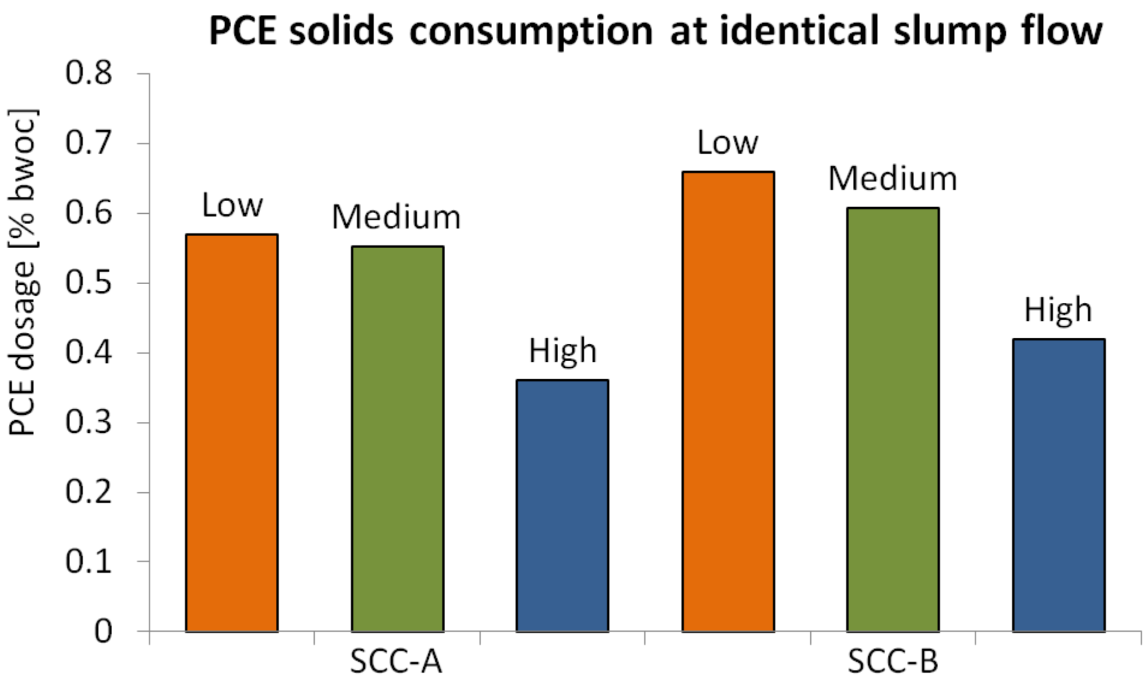


After Schober et al., 1997

Boundary framework

Spread flow correlates in a linear way with the adsorbed polymers at constant w/c.

The amount of adsorbed polymers at a time X is strongly controlled by the charge density.

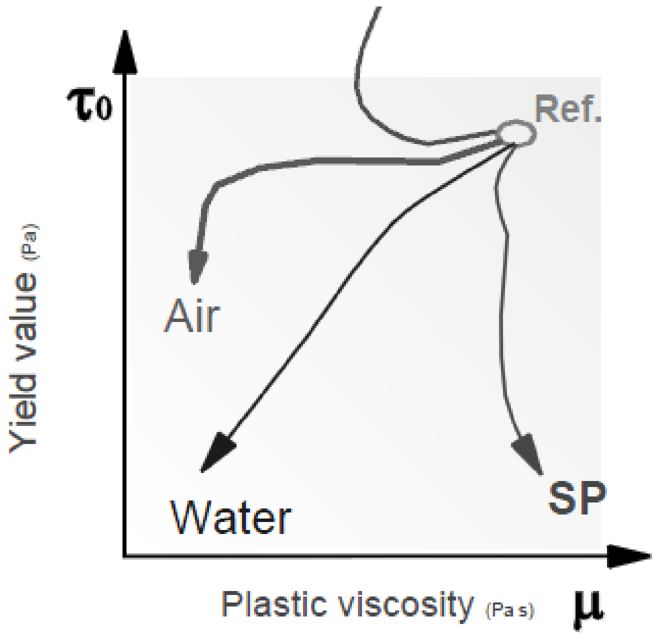


Boundary framework

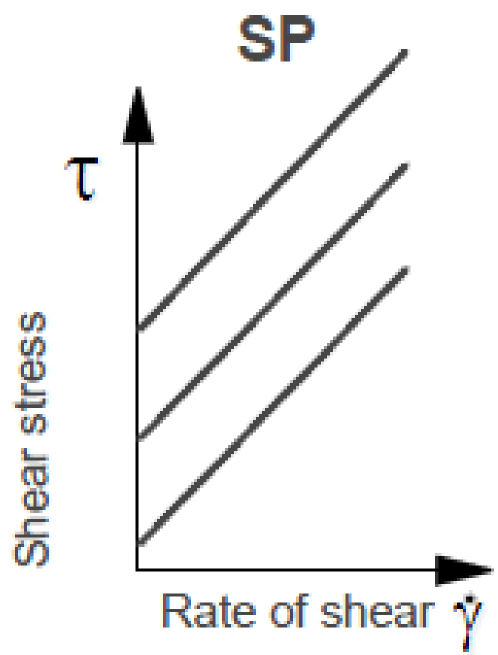
Spread flow correlates in a linear way with the adsorbed polymers at constant w/c.

The amount of adsorbed polymers at a time X is strongly controlled by the charge density

PCE adsorption mainly affects the yield stress.



Wallevik, 2006



Wallevik, 2006

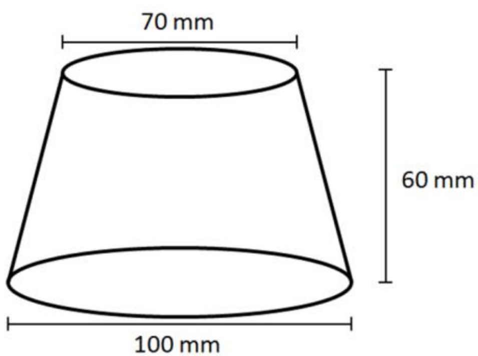
Boundary framework

Spread flow correlates in a linear way with the adsorbed polymers at constant w/c.

The amount of adsorbed polymers at a time X is strongly controlled by the charge density

PCE adsorption mainly affects the yield stress.

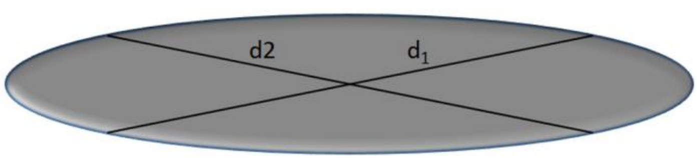
Slump flow diameter is predominantly affected by yield stress of a system.



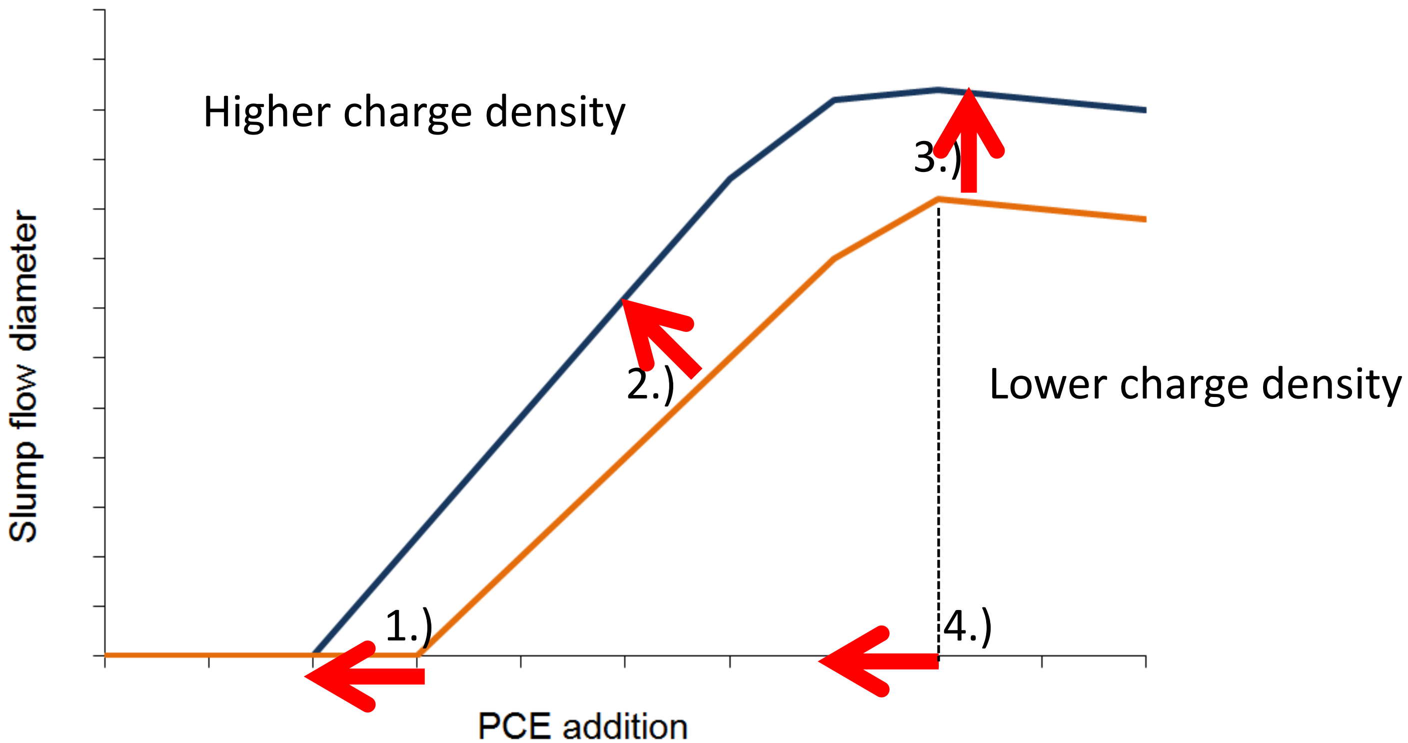
$$\tau_0 = \frac{225 \rho g V^2}{128 \pi^2 R^5}$$

Nicolas Roussel

$d_{SF} = (d_1+d_2)/2$



Interpretation



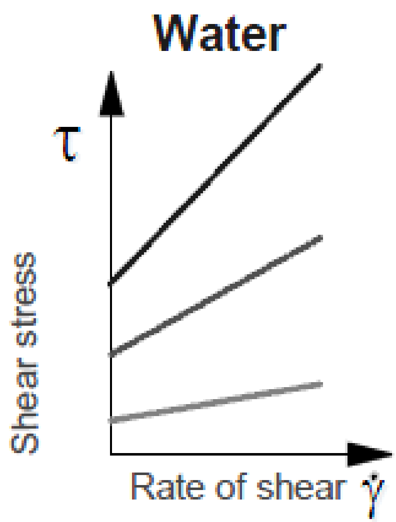
The observation can only be qualitative.

Mixture proportioning

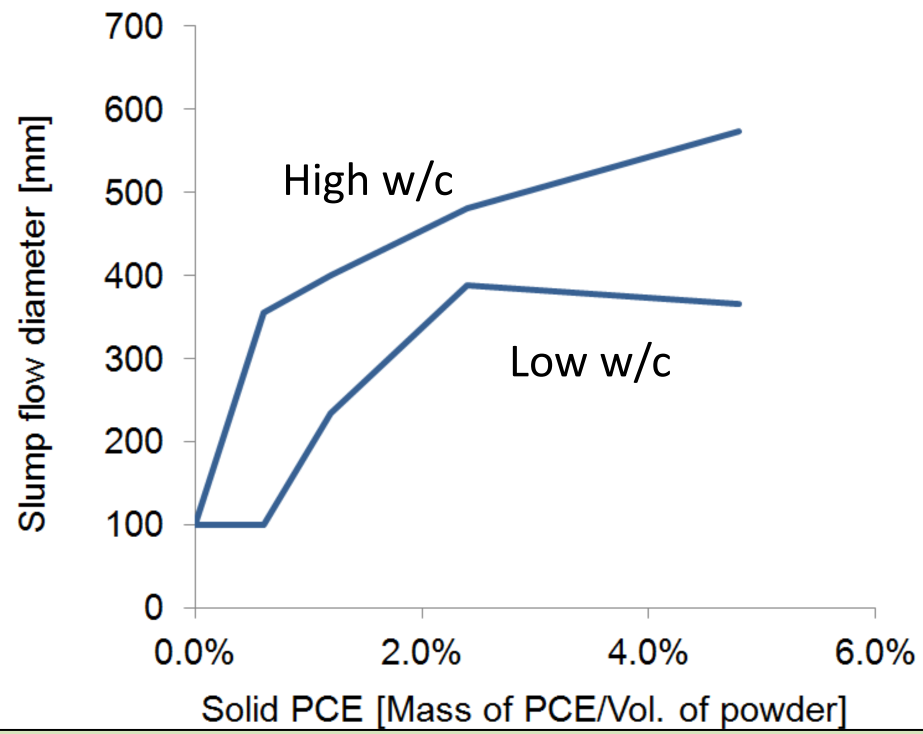
How to adjust the water to powder ratio?

The yield stress changes shall be induced predominatly by PCE.

Water blurs the interpretation of the curves.

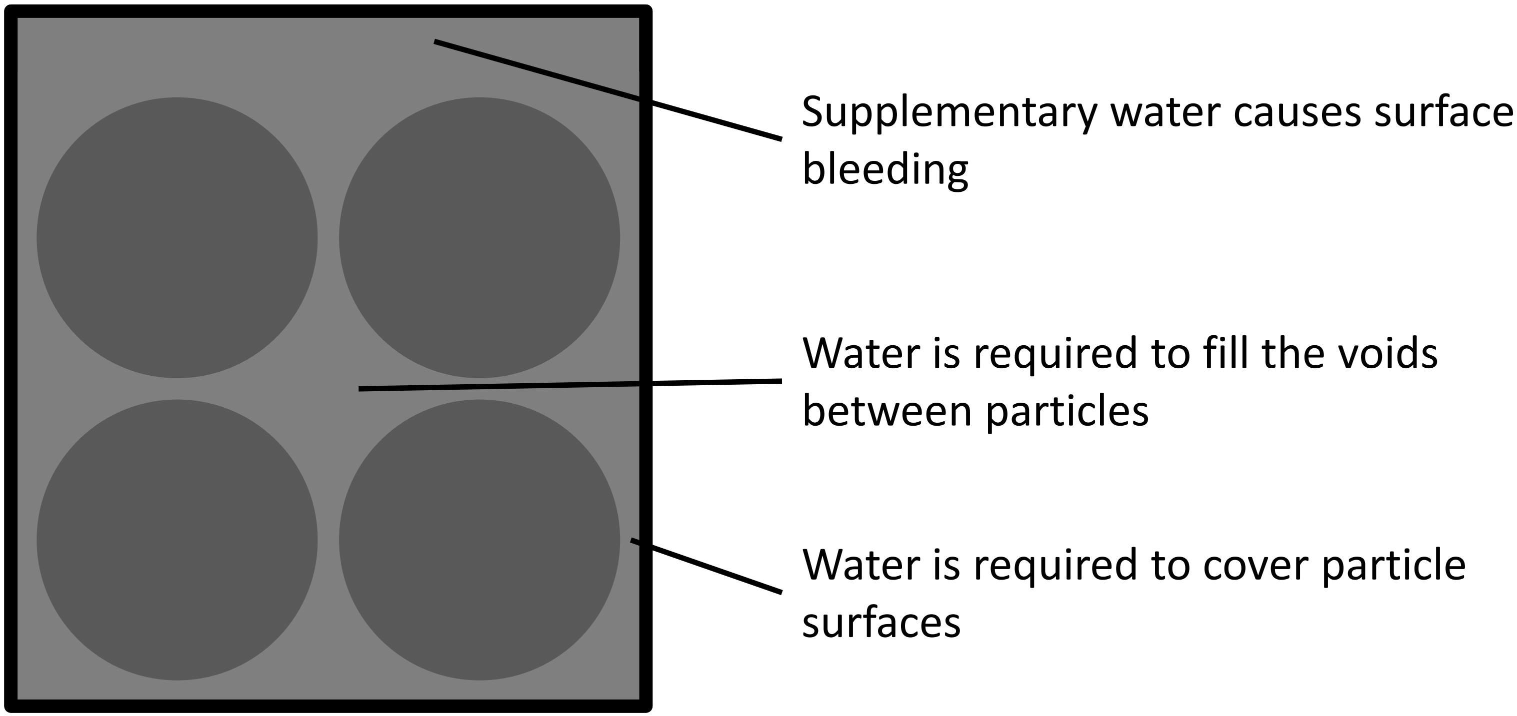


Wallevik, 2006



The system's water content shall be as low as possible!

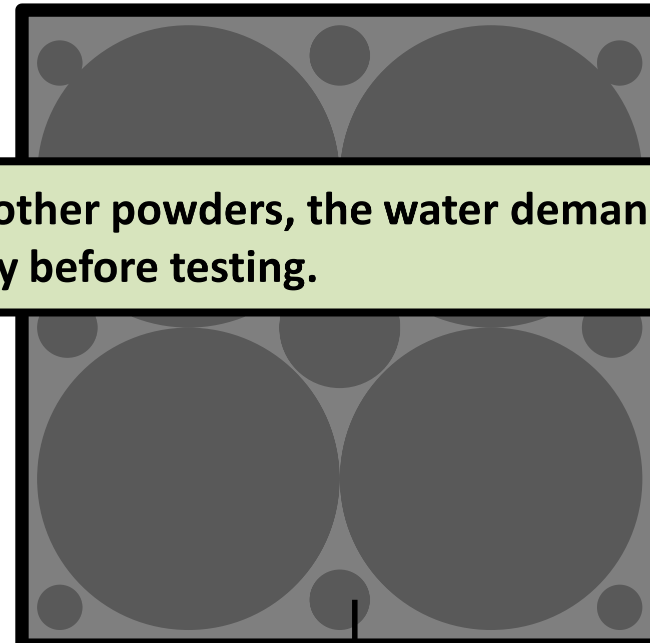
Puntke-test


Supplementary water causes surface bleeding
Water is required to fill the voids between particles
Water is required to cover particle surfaces

Mixture proportioning

Puntke-test

Due to different packing densities of cements or other powders, the water demand shall be determined individually before testing.

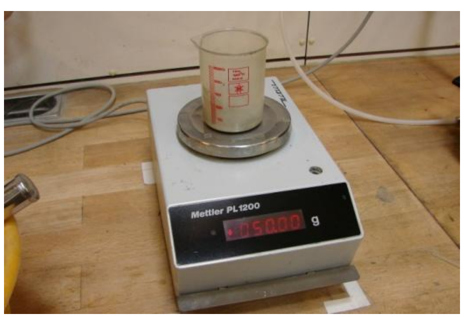


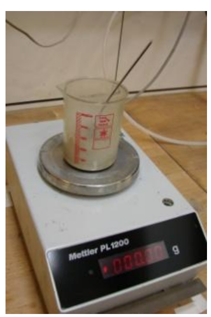
Poor packing density = high water demand

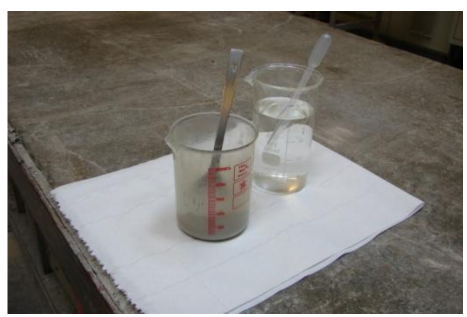
High packing density = low water demand

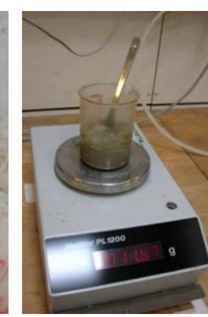
Puntke-method to determine water demand of one powder

- Weigh in powder (50 g – 100 g) into a beaker and note the value.
- Put spoon or similar into beaker and tare balance.
- Continuously add water drop by drop, and stirr/agitate
- until the required consistency is achieved.
- Put beaker + spoon + material + water on balance.
- n_w = (Final reading/1.0) / (First note/ρ_P + Final reading/1.0)
- Use different starting weights in order to avoid „self-cheating“.
- In order to accelerate the process, a vibration table can be used.









Mixture proportioning:

PCEs typically contain water contents between 65% and 80%.

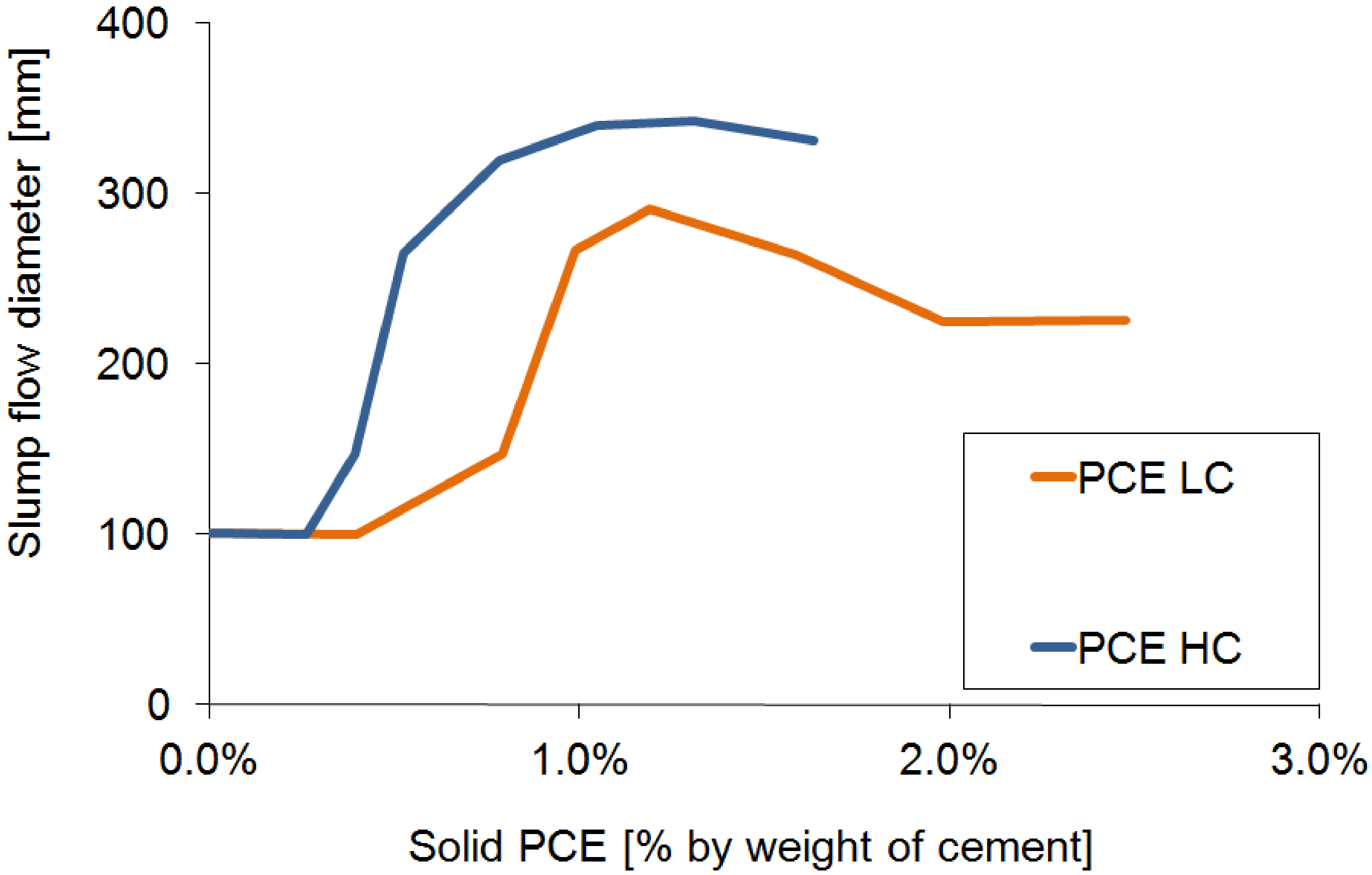
Maximum PCE dosages can be in the range of 3%-4% bwoc → significant w/c increase.

Component	Unit	Ratios	Density[kg/m³]	Mixtures for test series with varied PCE contents				
PCE	[% bwo powder]		1070	0%	1%	2%	3%	4%
PCE_{Dry} [1]	[% bwo PCE]	30%	-	0	4.5	9	13.5	18
$Water_{PCE}$ [1]	[% bwo PCE]	70%	1000	0	10.5	21.0	31.5	42.0
$Total_{PCE}$ [1]	[% bwo PCE]	70%	1000	0	15.0	30.0	45.0	60.0
Cement	[g]		3120	1500	1500	1500	1500	1500
Water addition	[g]		1000	378	367	357	346	336
total water[2]	[g]	44%[3]		378				
PCE_{Solids}	[% by weight]			0.00%	0.30%	0.60%	0.90%	1.20%
	[$weight._{PCE}$/$vol._{Cement}$]			0.00%	0.94%	1.87%	2.81%	3.74%

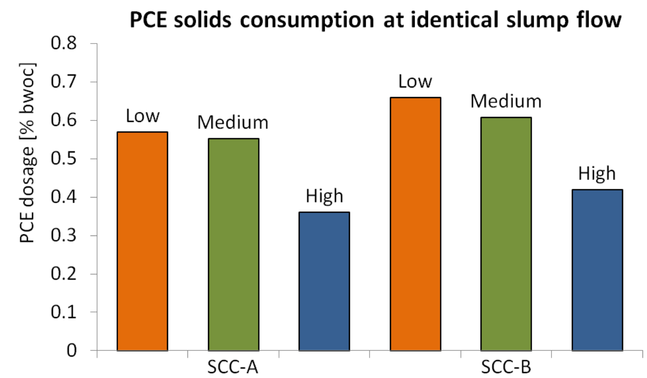
Each test with varied PCE dosage needs a new mix!!!

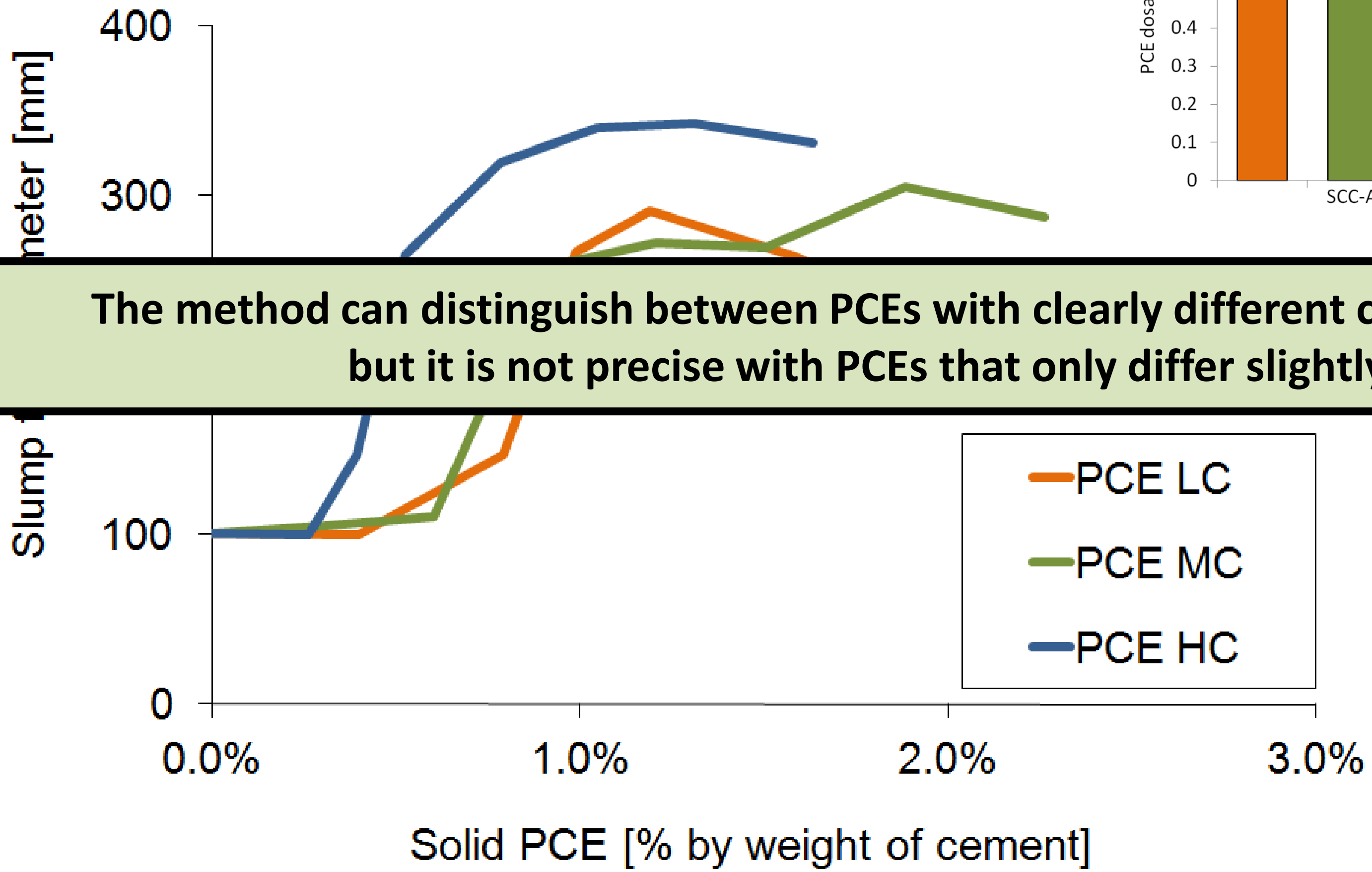
Discussion of results

Experimental results:



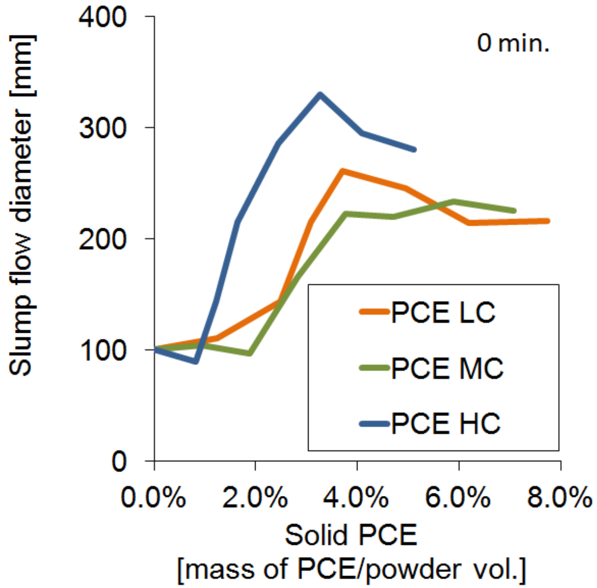
Experimental results:

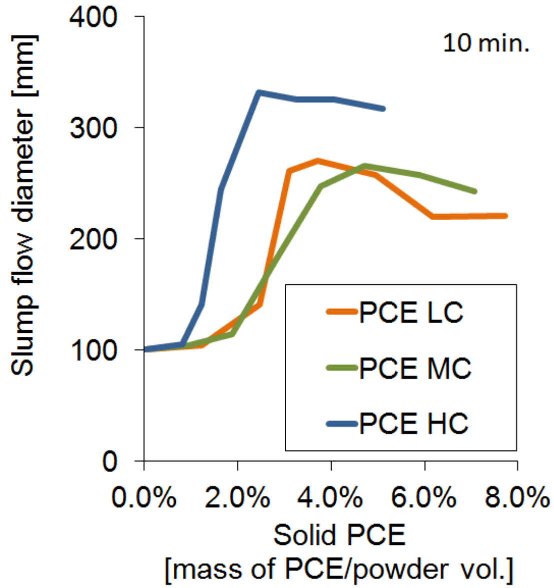


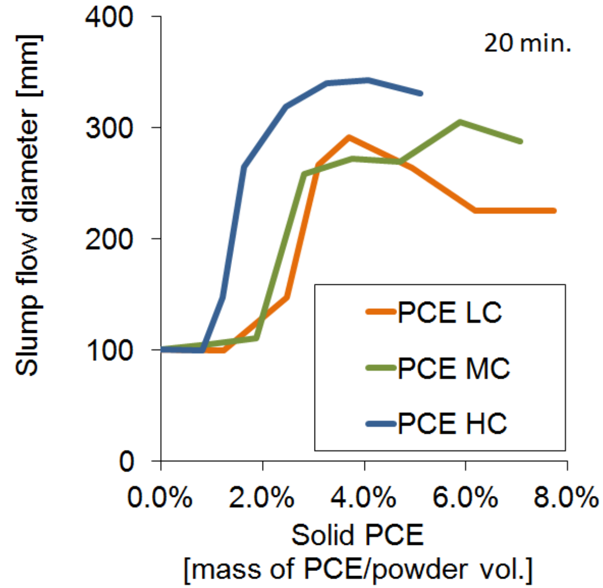


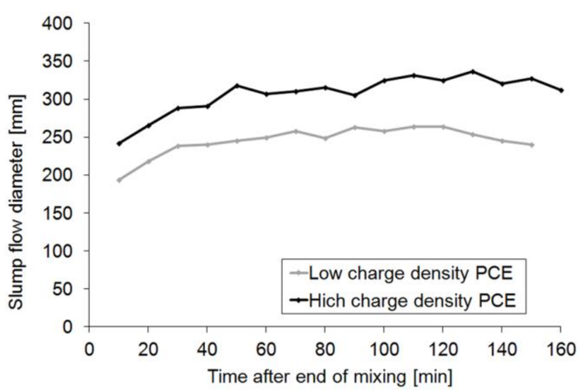
The method can distinguish between PCEs with clearly different charge density, but it is not precise with PCEs that only differ slightly.

Influence of observation time:



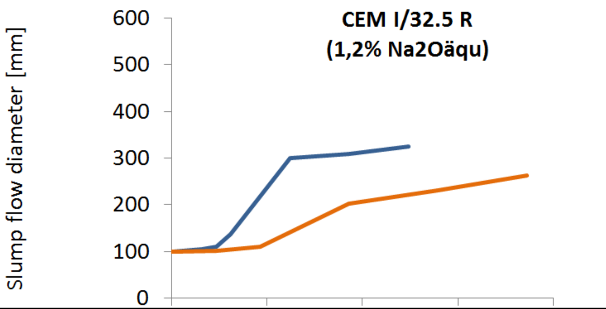


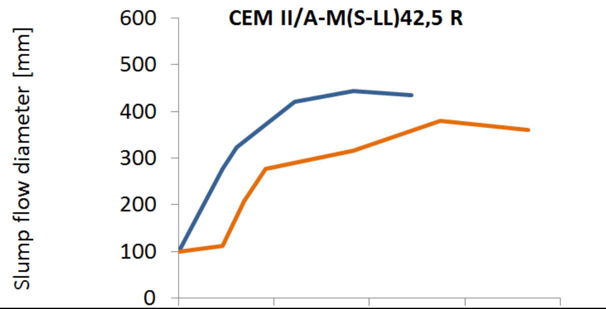




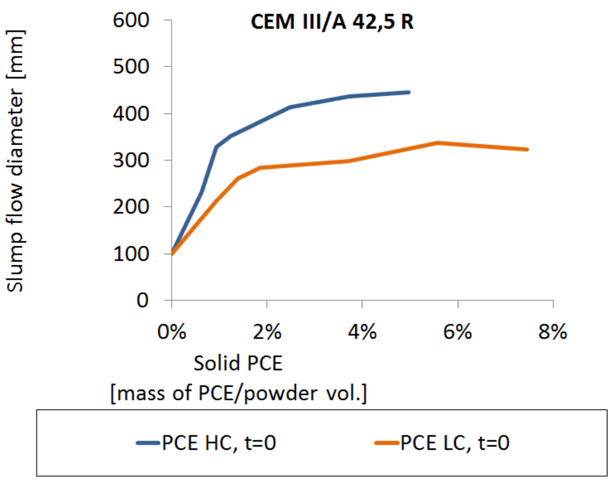
Time effects are negligible

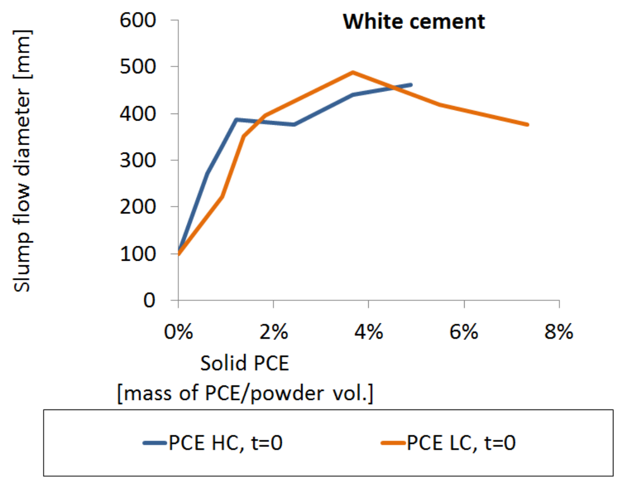
Use with varied cement types:



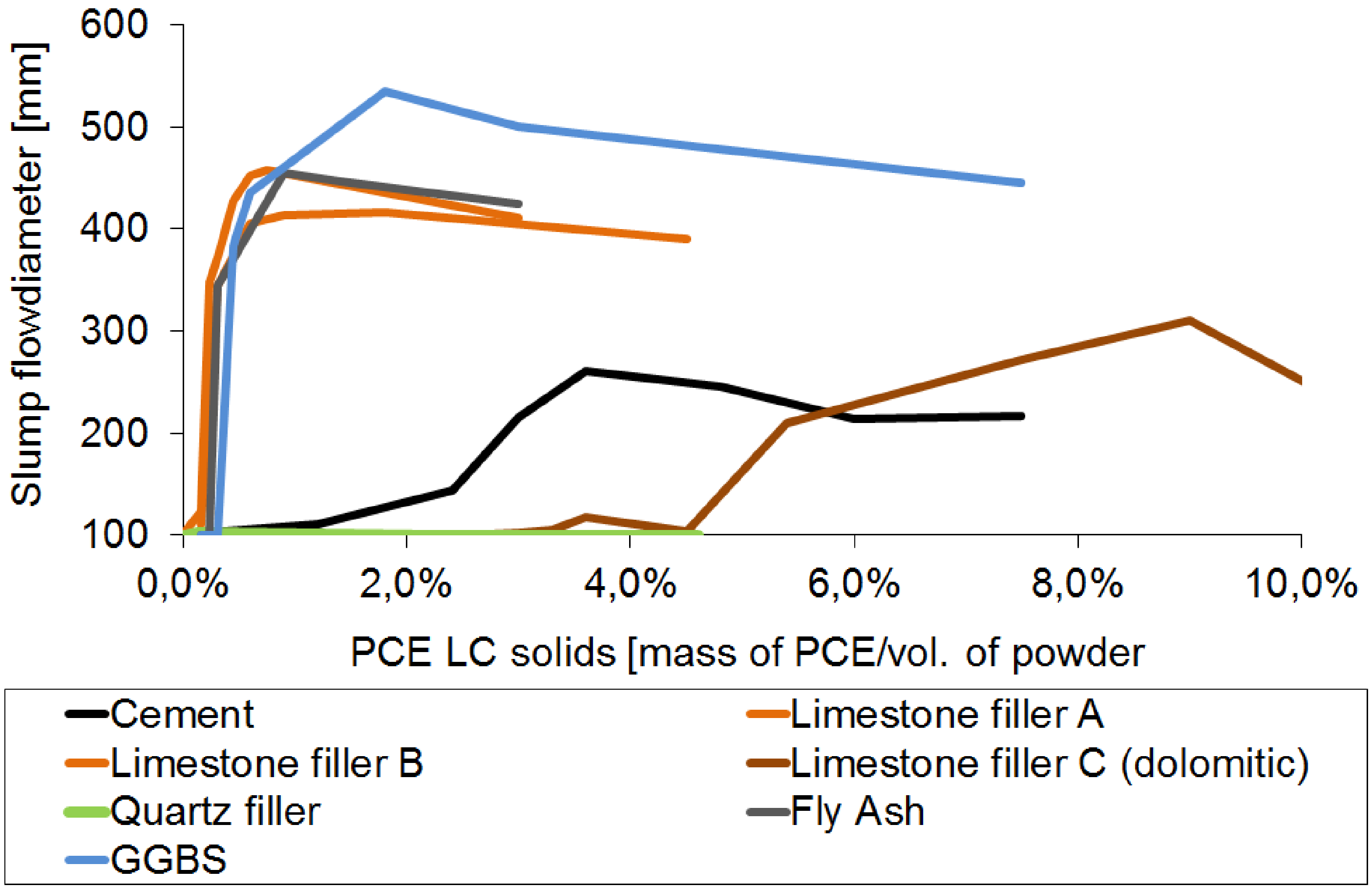


The method functions regardless of the cement type.





Applicability with other powders than cement



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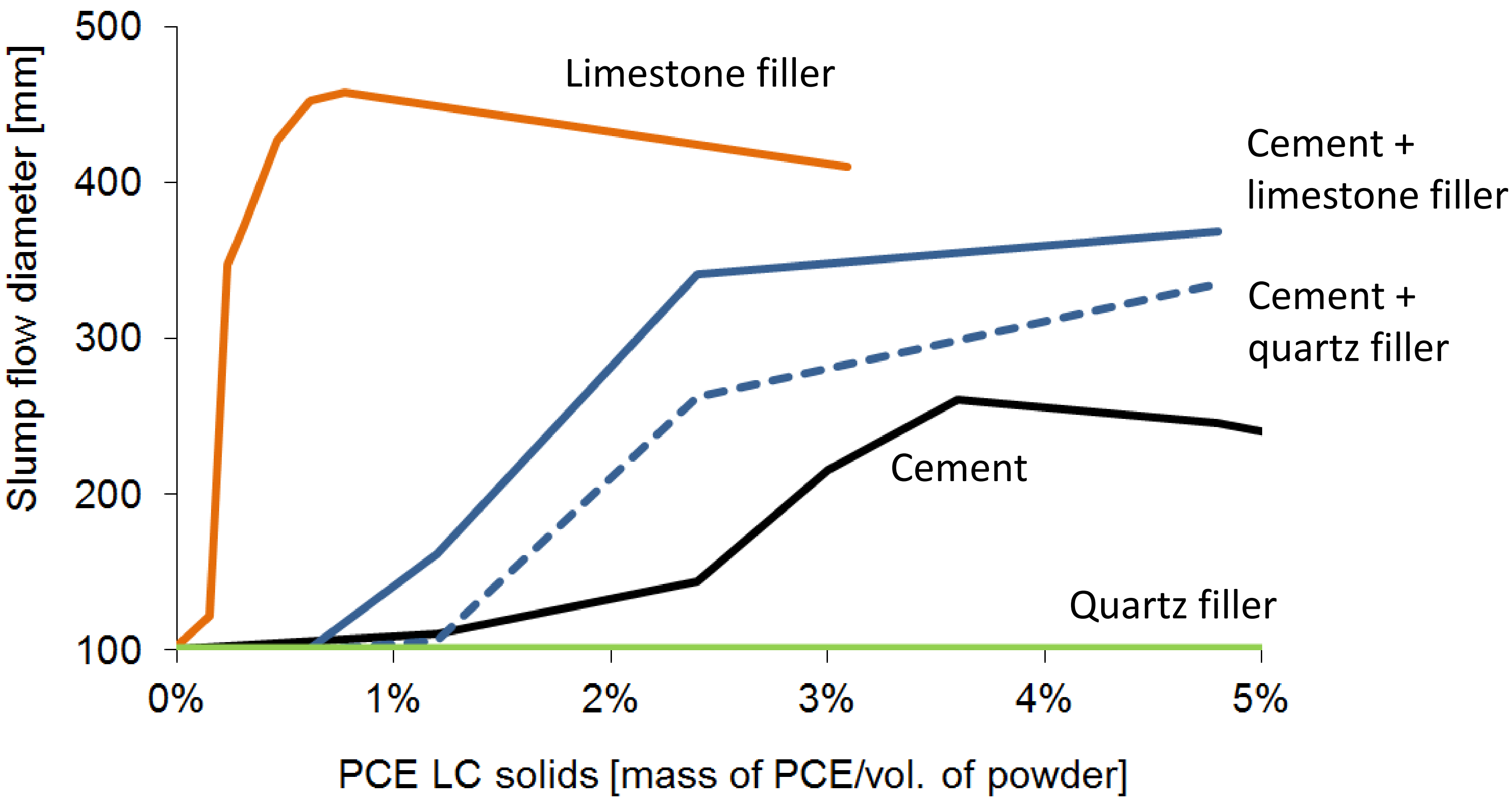

Use with powder mixes

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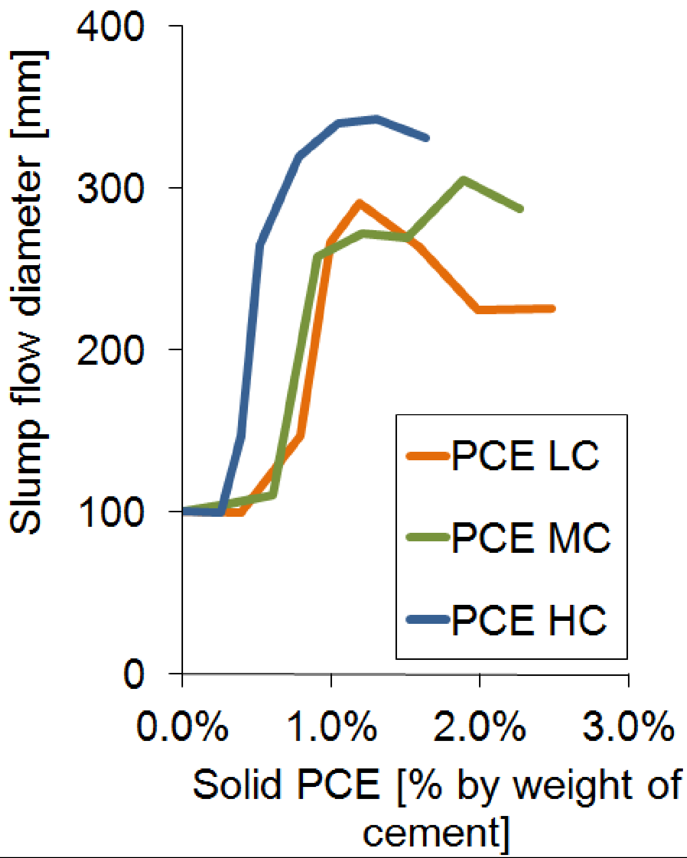
total water[2]	[g]	44%[3]		378				
PCE_{Solids}	[% by weight]			0.00%	0.30%	0.60%	0.90%	1.20%
	[$weight._{PCE}/vol._{Cement}$]			0.00%	0.94%	1.87%	2.81%	3.74%

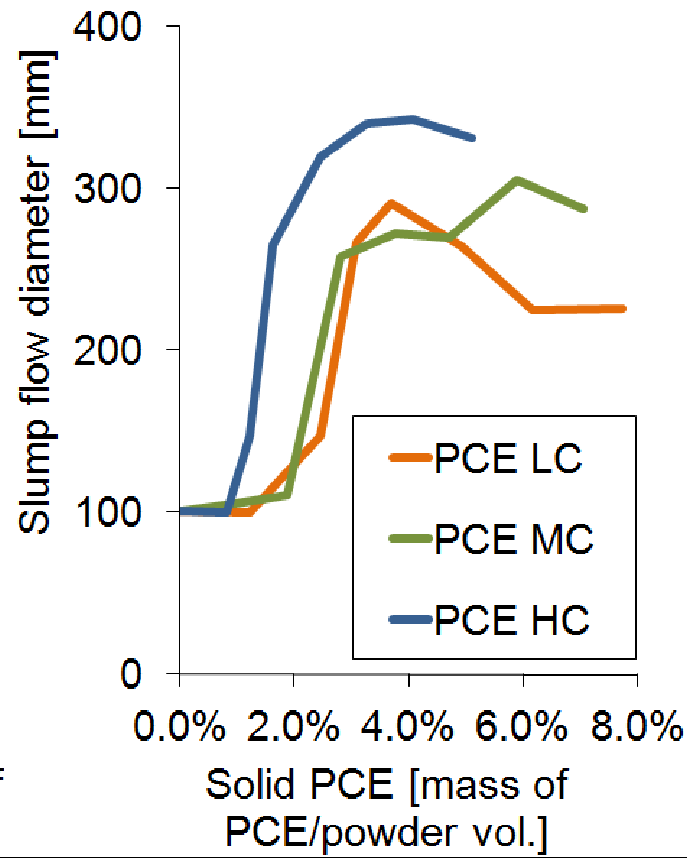
[1]PCE solid content = 30%

[2]PCE compound density = 1.07 g/m³

[3]Water demand of cement mixture according to the Puntke test = 0.44

Use with powder mixes:





With one powder the spread diameter can be plotted against PCE content in weight %. For more powders, it is reasonable to plot the weight of PCE vs. the volume of powders.

Summary

Summary

- A simple method was proposed to qualitatively distinguish PCEs by their adsorption behaviour/charge density.
- The method is based on the assumption that differently charged PCEs yield a shift of characteristic spots in the curve that is generated by plotting the spread flow vs. the PCE dosage.
- The method can distinguish PCEs which show large differences in their charge densities. If the charge densities are similar, the method might not be sensitive enough.
- The method works with any cement and also powder blends.
- It helps to identify „threshold" PCEs, which should suffice to achieve any required performance specification.

Thank you for your kind attention!