


02.03.2016



INFLUENCE OF EFFECTS ON NANO AND MICRO SCALE ON THE RHEOLOGICAL PERFORMANCE OF CEMENT PASTE, MORTAR AND CONCRETE

Wolfram Schmidt

BAM Bundesanstalt für Materialforschung und -prüfung





Introduction



Necessity to understand rheology of concrete

Casting is by far the highest source for failure at hardened state.

- Tailored and robust workability ensures durability

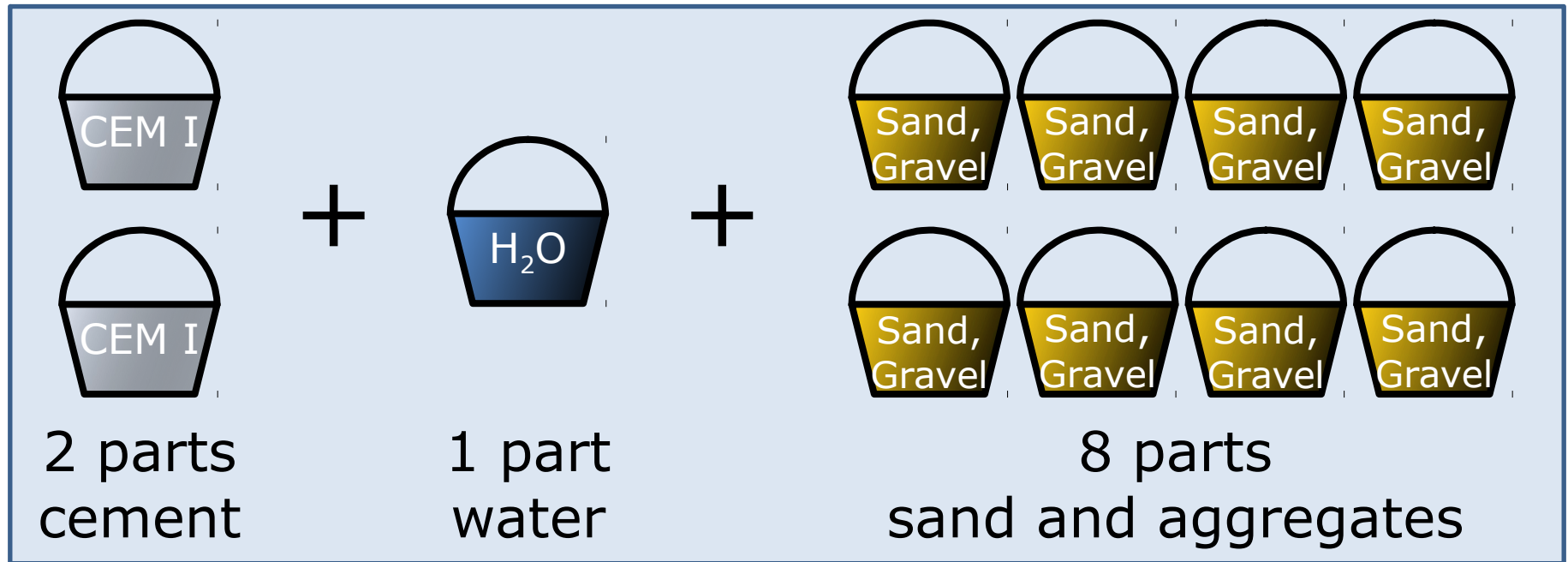
Rheology is key for:

- **safe application**
- **durable performance**
 - **sustainability**
 - **innovation**

Introduction

Concrete in the past

- Sound functionality
- Simplicity



Concrete in the past and future options

Many people wish back the „good“ (???) old times:

- Only ordinary portland cement
- w/c and cement content determine the strength and durability
- Believe in an unalterable 28-d compressive strength value

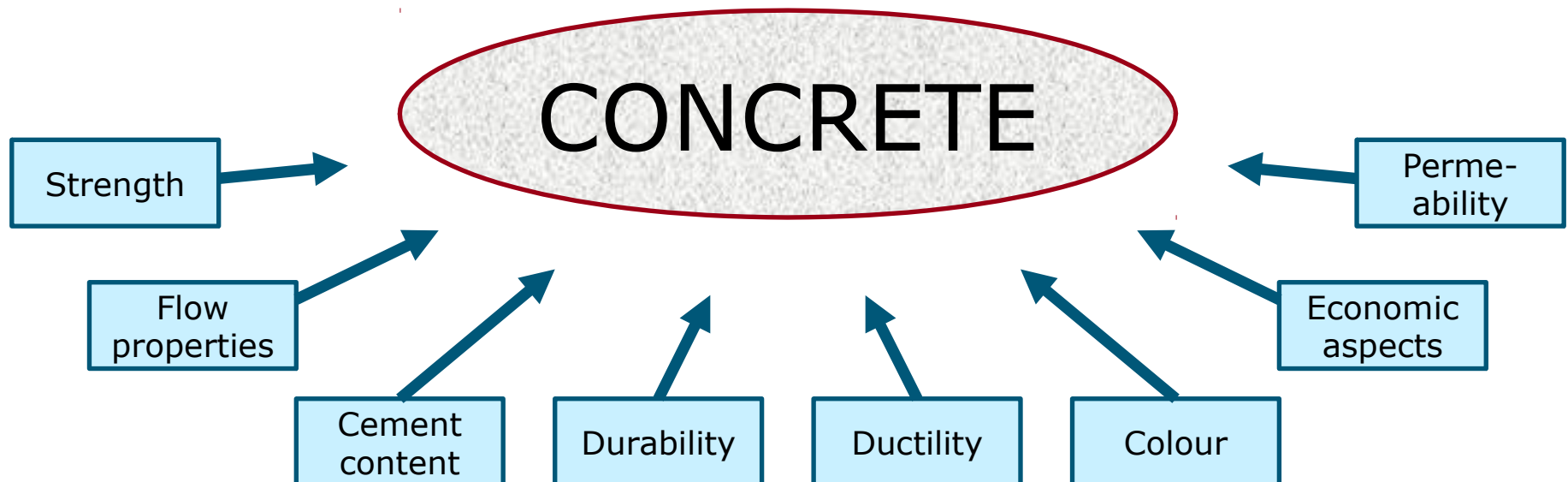
We must not forget:

- At business as usual, cement will be responsible for 1/3 of the global CO₂ emissions in 2050. (A blueprint for a climate friendly cement industry, 2008)
- We have to develop more economically and environmentally friendly technologies.
- We want to master the challenges of the future.

Introduction

Concrete today

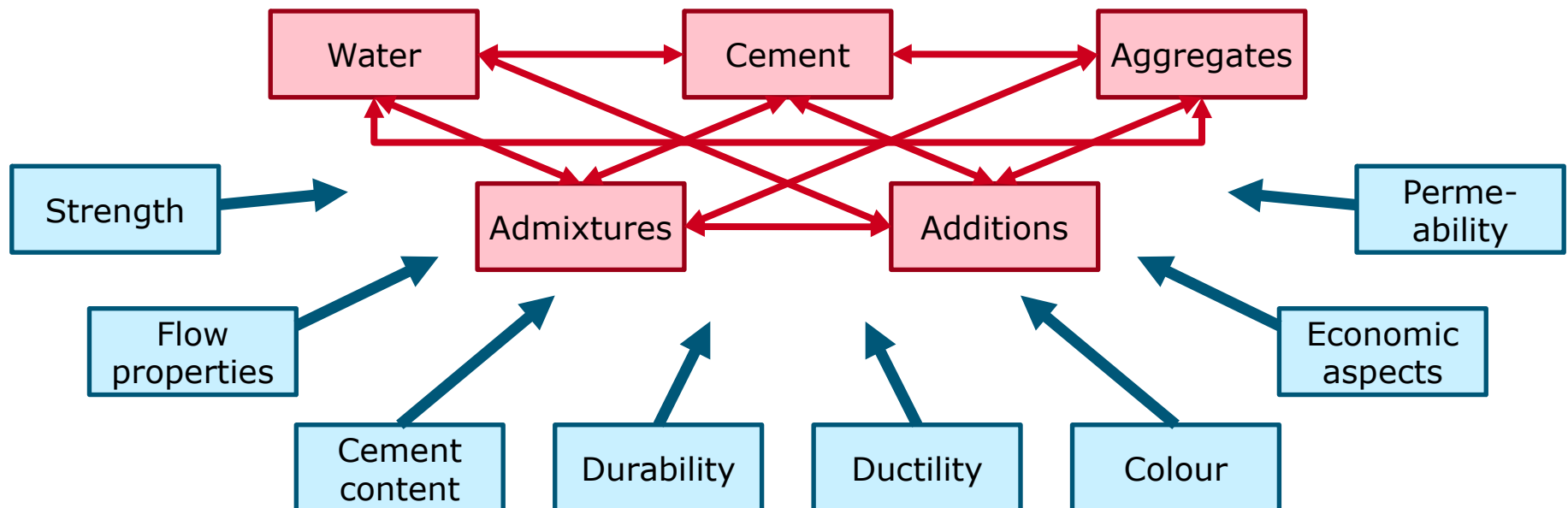
- Regarding performance specifications of concrete, there should not be any limits today.



Introduction

Concrete today

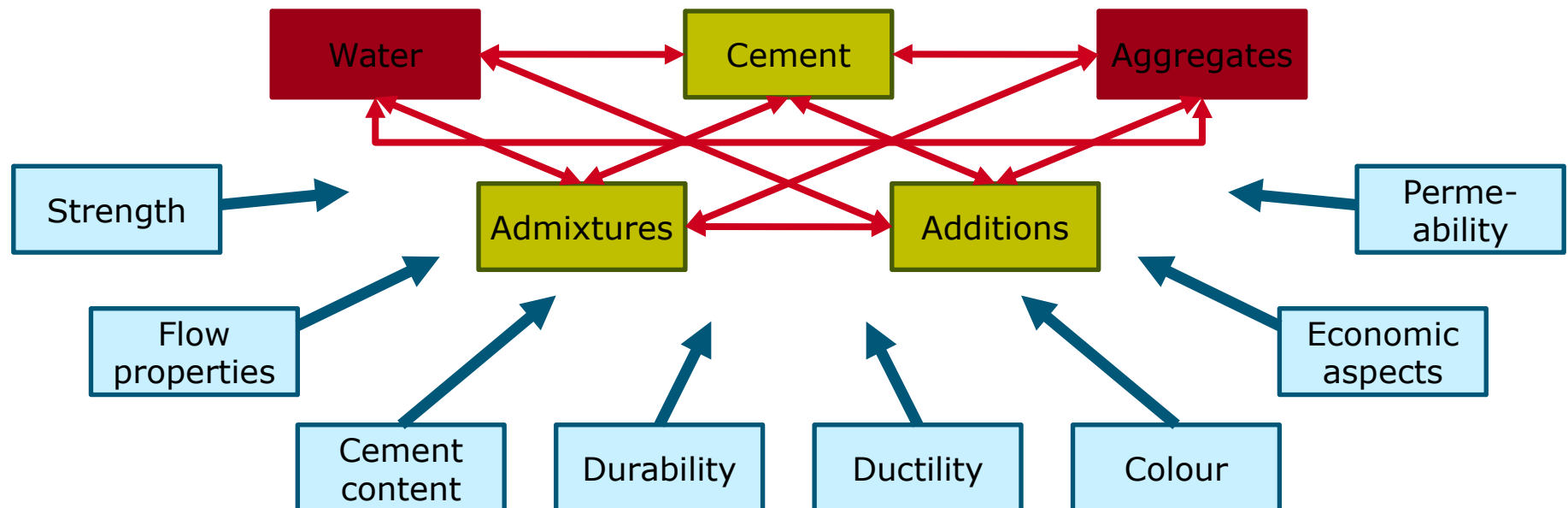
- Regarding performance specifications of concrete, there should not be any limits today.
- Mix design has become more complex due to multiple parameters.



Introduction

Concrete today

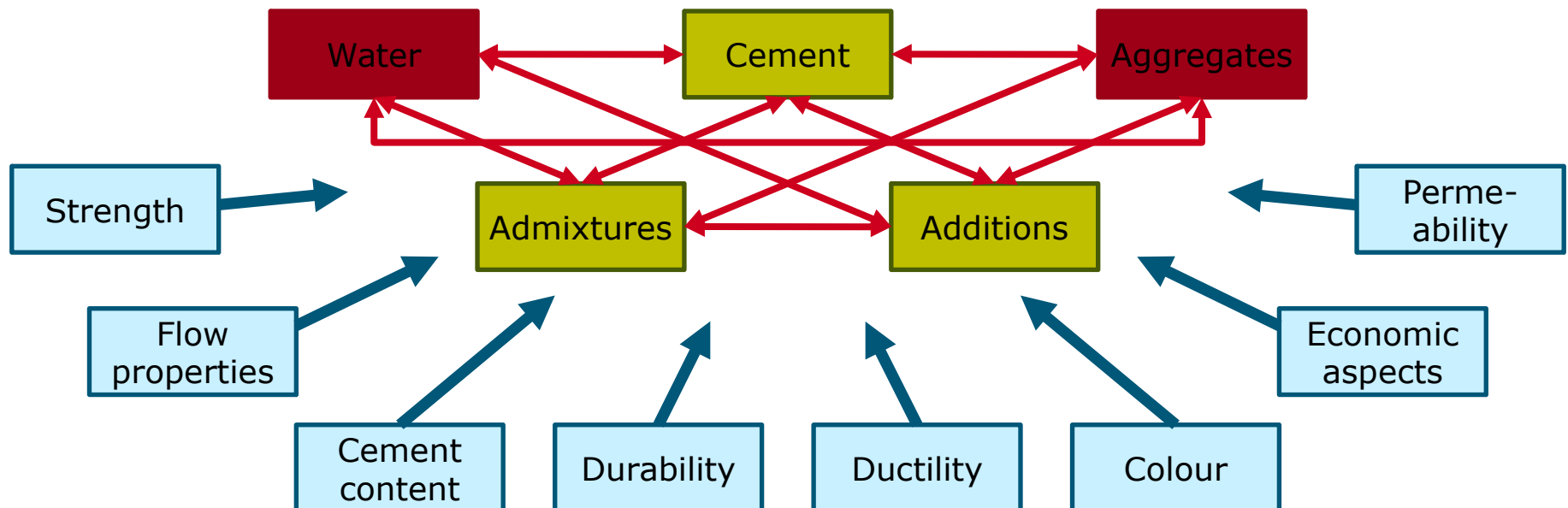
- Regarding performance specifications of concrete, there should not be any limits today.
- Mix design has become more complex due to multiple parameters.
- The new challenges in the „mix design“ are below powder size.



Introduction

Concrete today

- Regarding performance specifications of concrete, there should not be any limits today.
- Mix design has become more complex due to multiple parameters.
- The new challenges in the „mix design“ are below powder size.





Influences of nano effects on the macroscopic rheology of concrete

Superplasticizers mainly affect the yield stress.



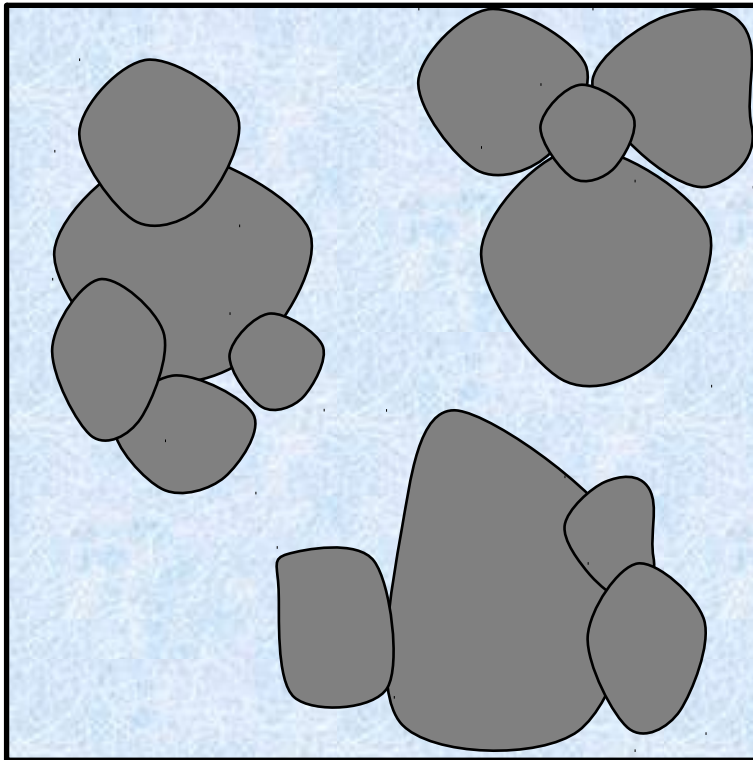
Concrete without SP.



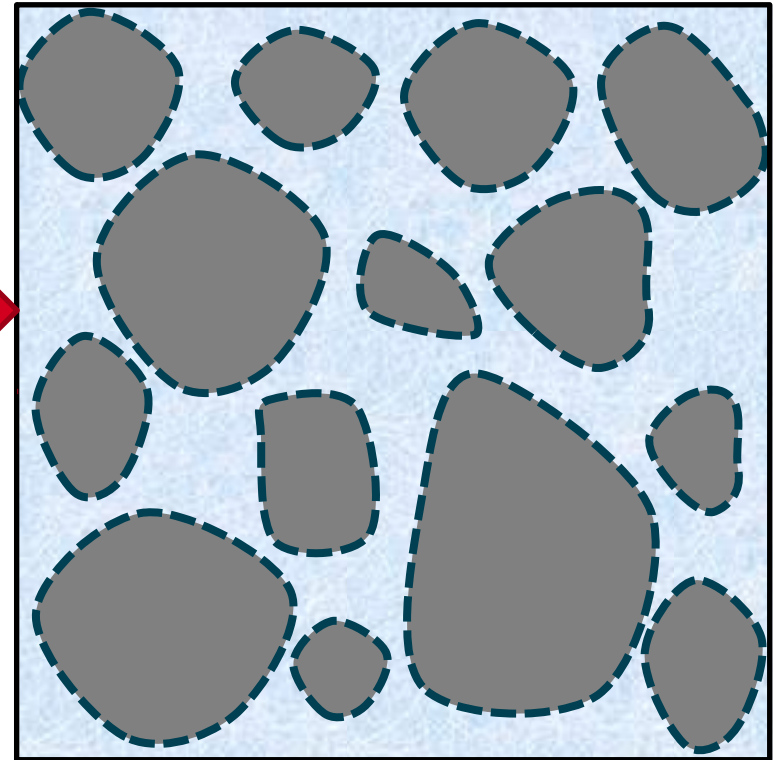
Identical concrete with PCE
($\approx 0.7\%$ bwo cement, or 0.096% bwo concrete)

Superplasticizers mainly affect the yield stress by adsorption which creates dispersion forces.

Normal concrete



Flowable Concrete

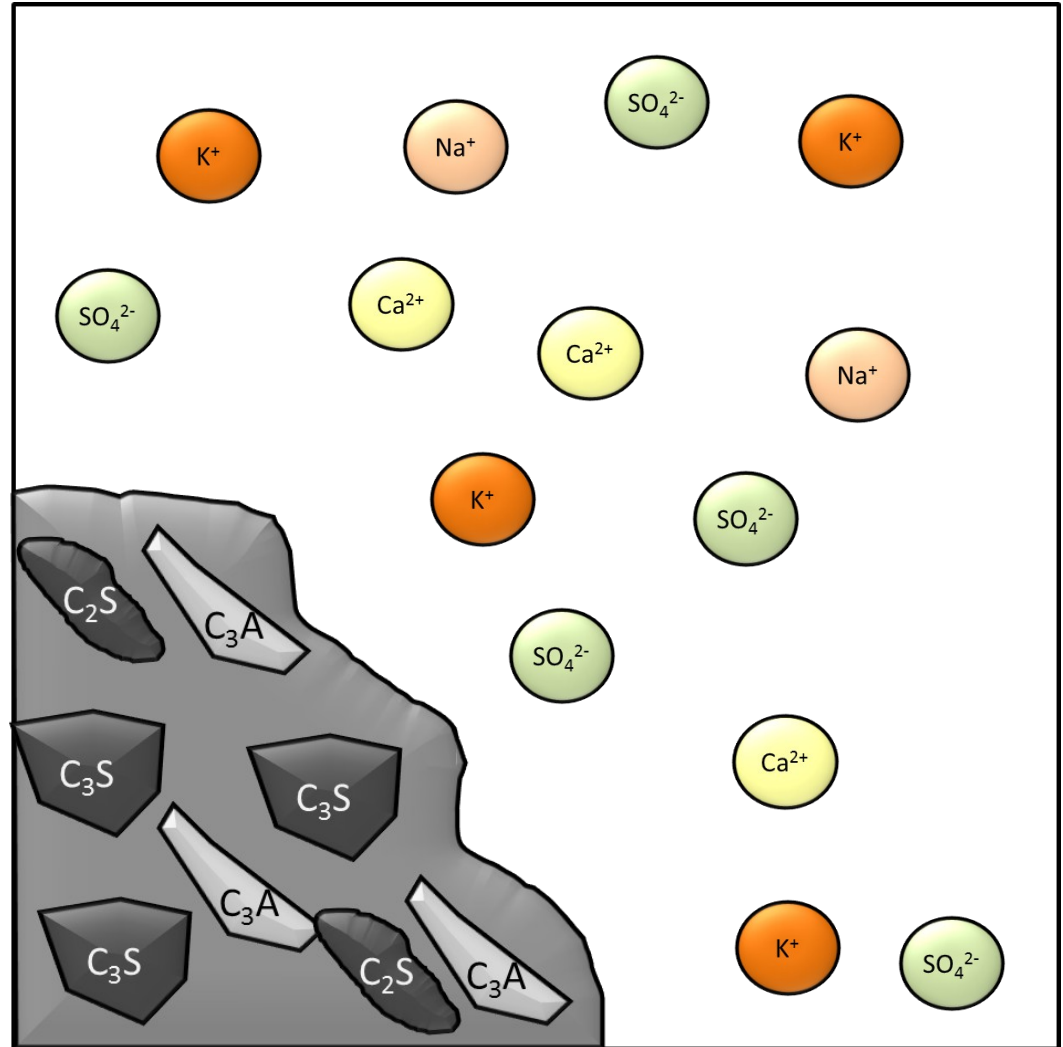


Rheology effects

Early cement hydration

Upon addition of water ions are dissolved:

- Sodium
- Potassium
- Calcium
- Sulphate

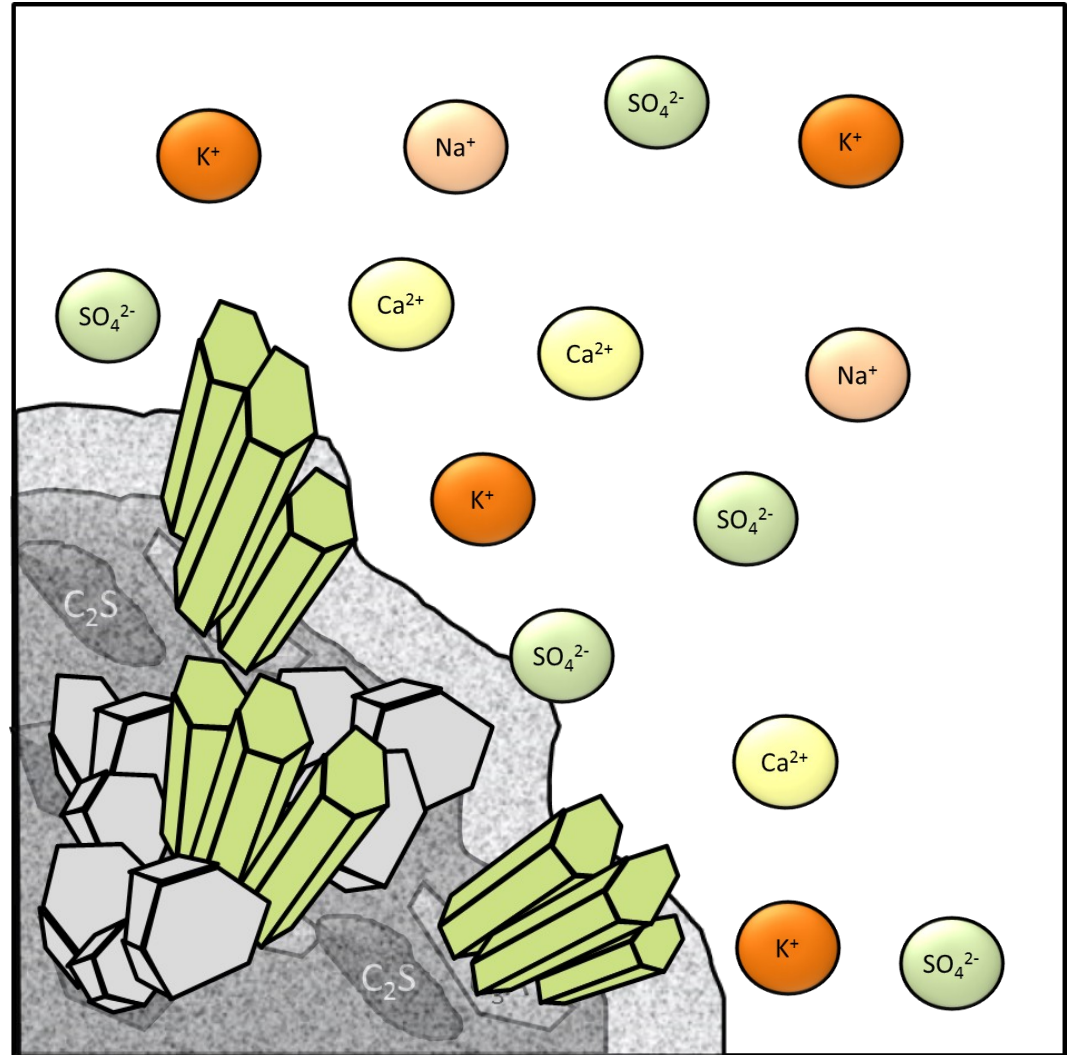


Rheology effects

Early cement hydration

First hydration phases:

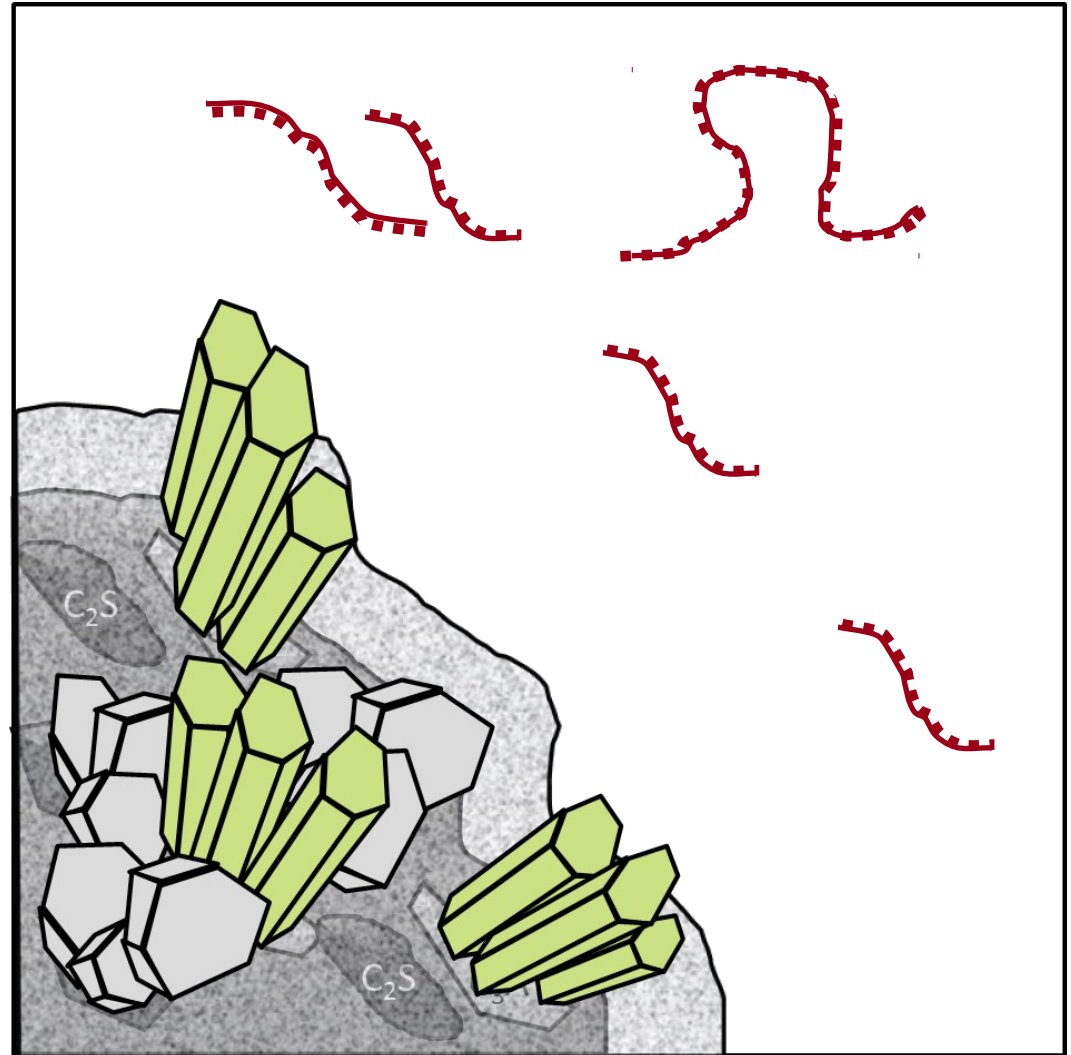
- C-S-H
- Portlandite
- Ettringite



Rheology effects

Early cement hydration

With PCE in the pore solution a number of effects occur in parallel:

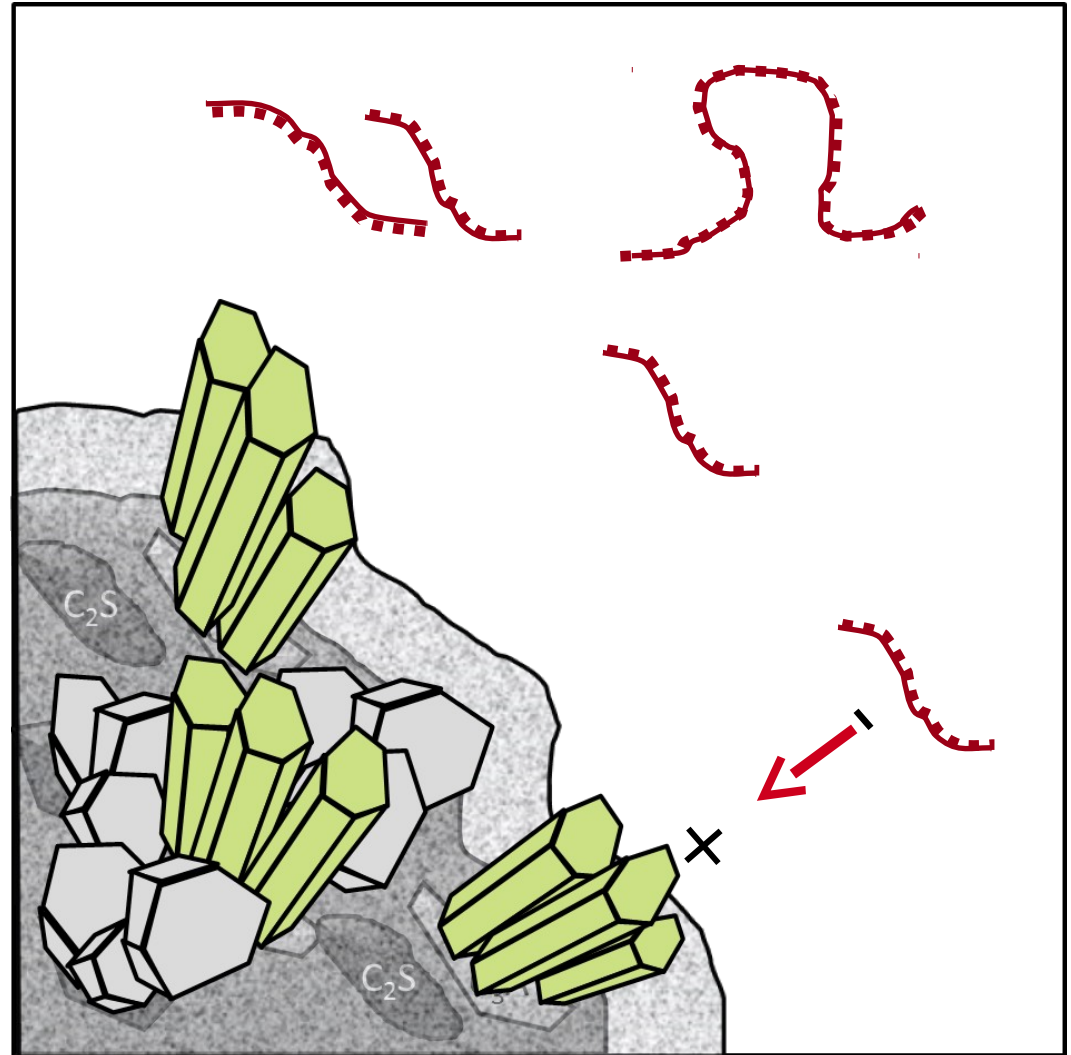
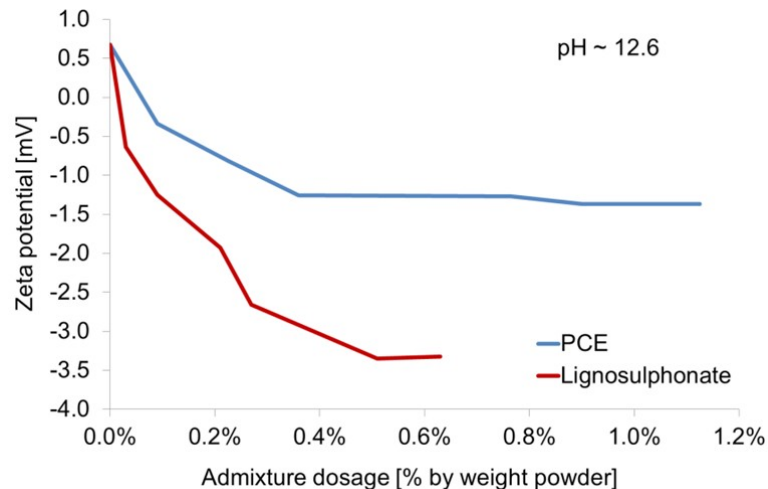


Rheology effects

PCE adsorption

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption

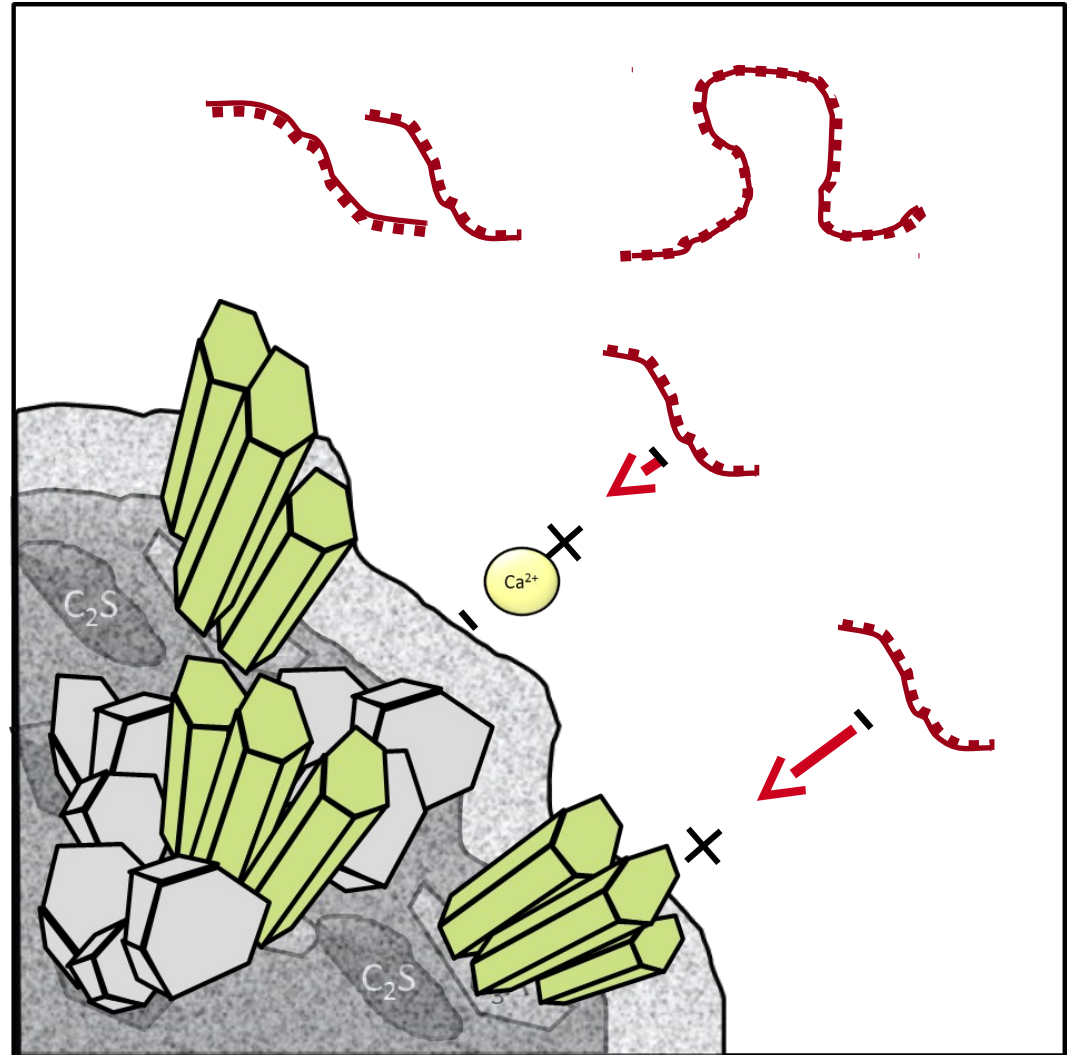


Rheology effects

Role of the cations

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption
- or via counter ions

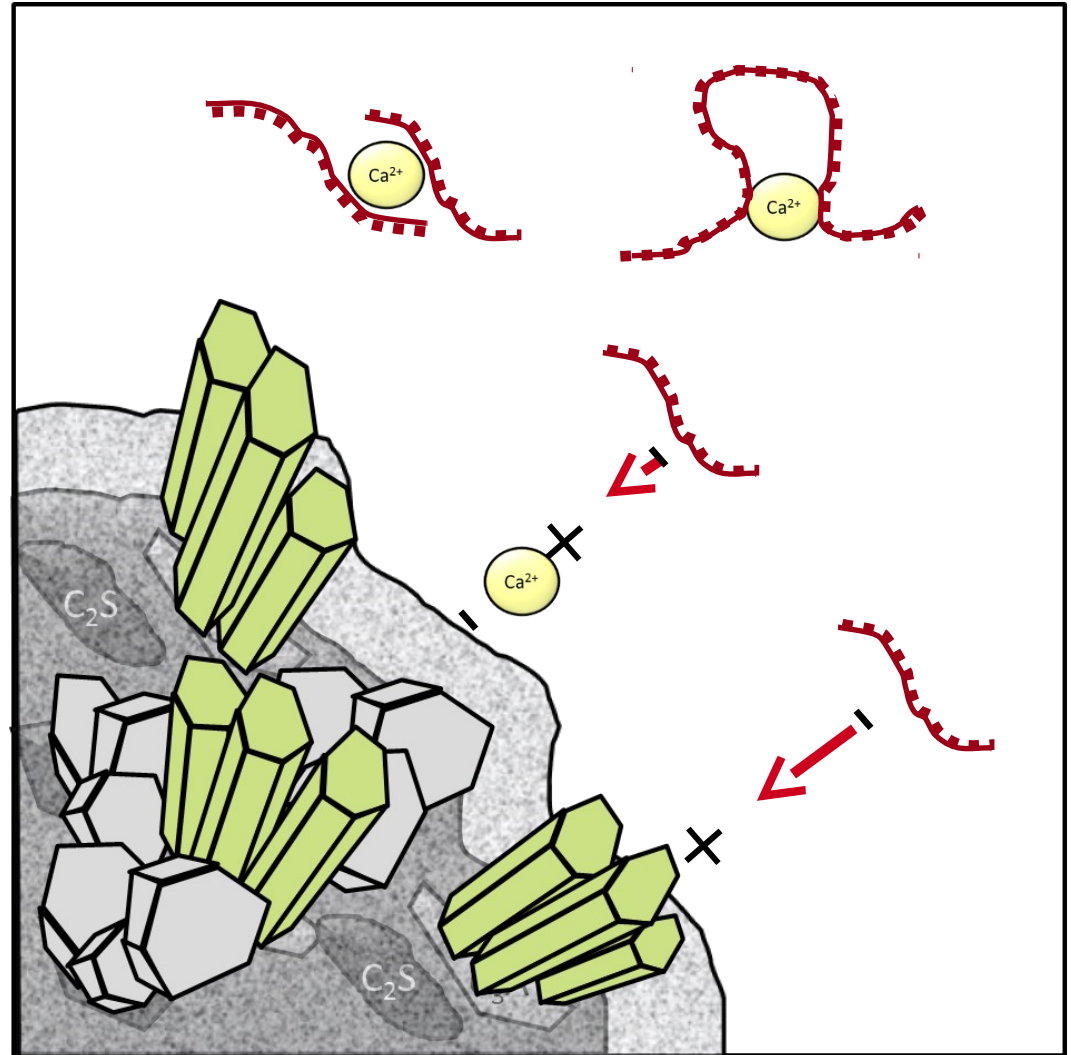
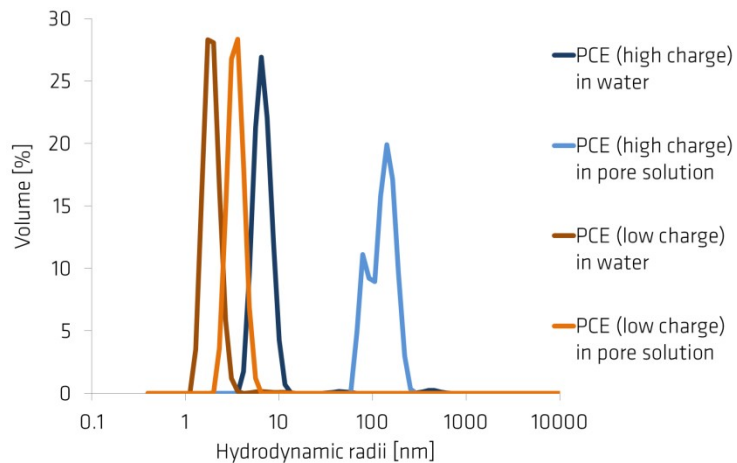


Rheology effects

Role of the cations

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption
- or via counter ions
- Cross linking via Ca^{2+}

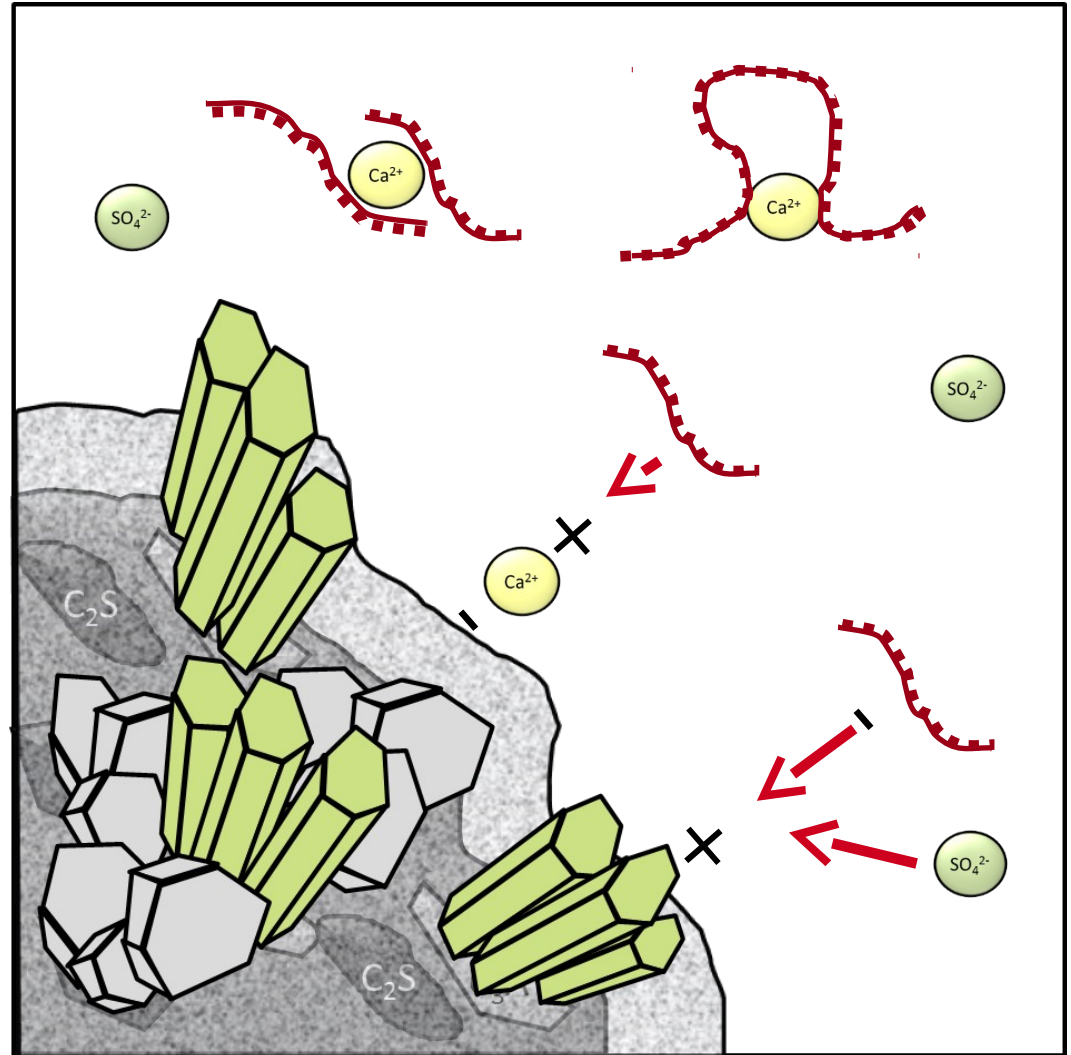


Rheology effects

Role of the anions

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption
- or via counter ions
- Cross linking via Ca^{2+}
- Competitive adsorption

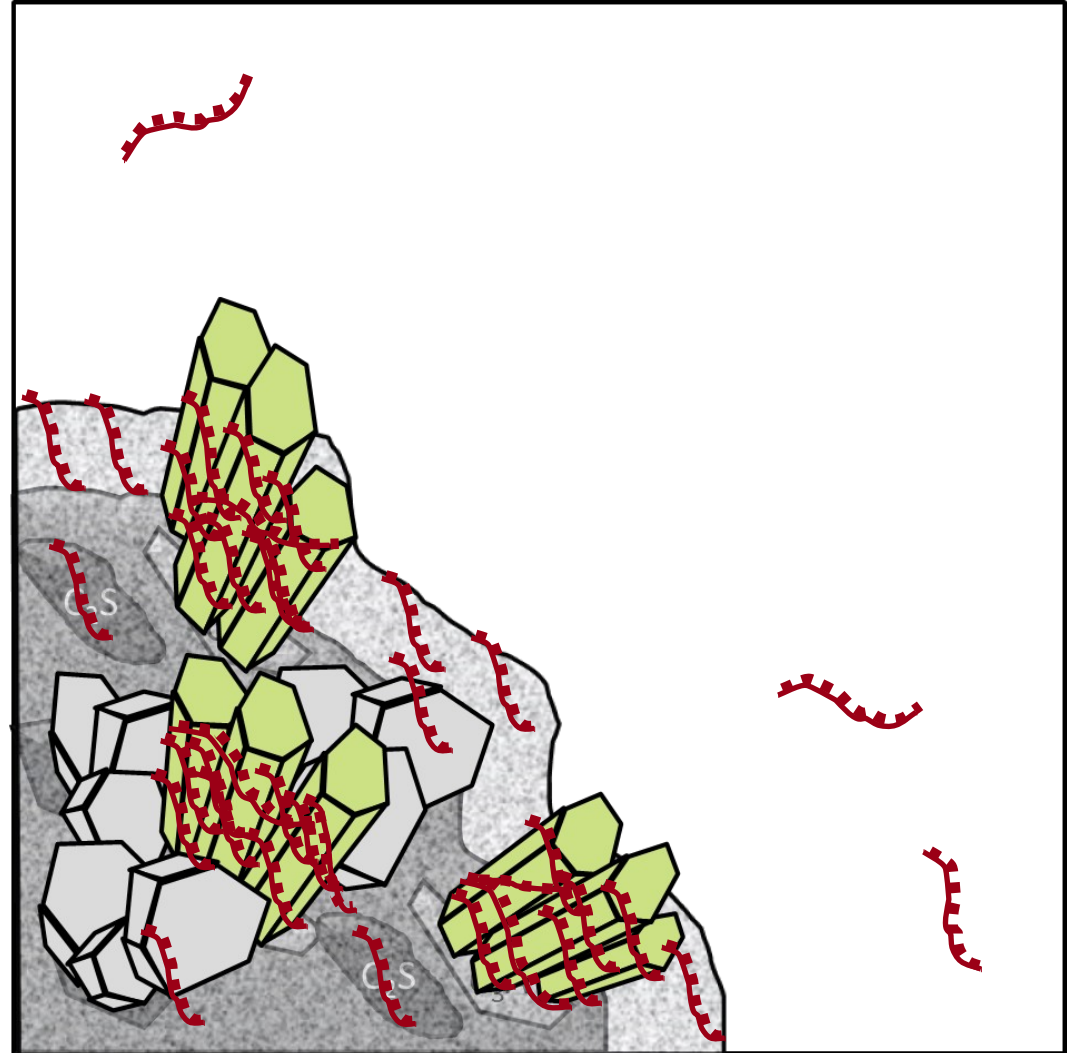


Rheology effects

Time effects

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption
- or via counter ions
- Cross linking via Ca^{2+}
- Competitive adsorption
- Not all polymers are adsorbed immediately.

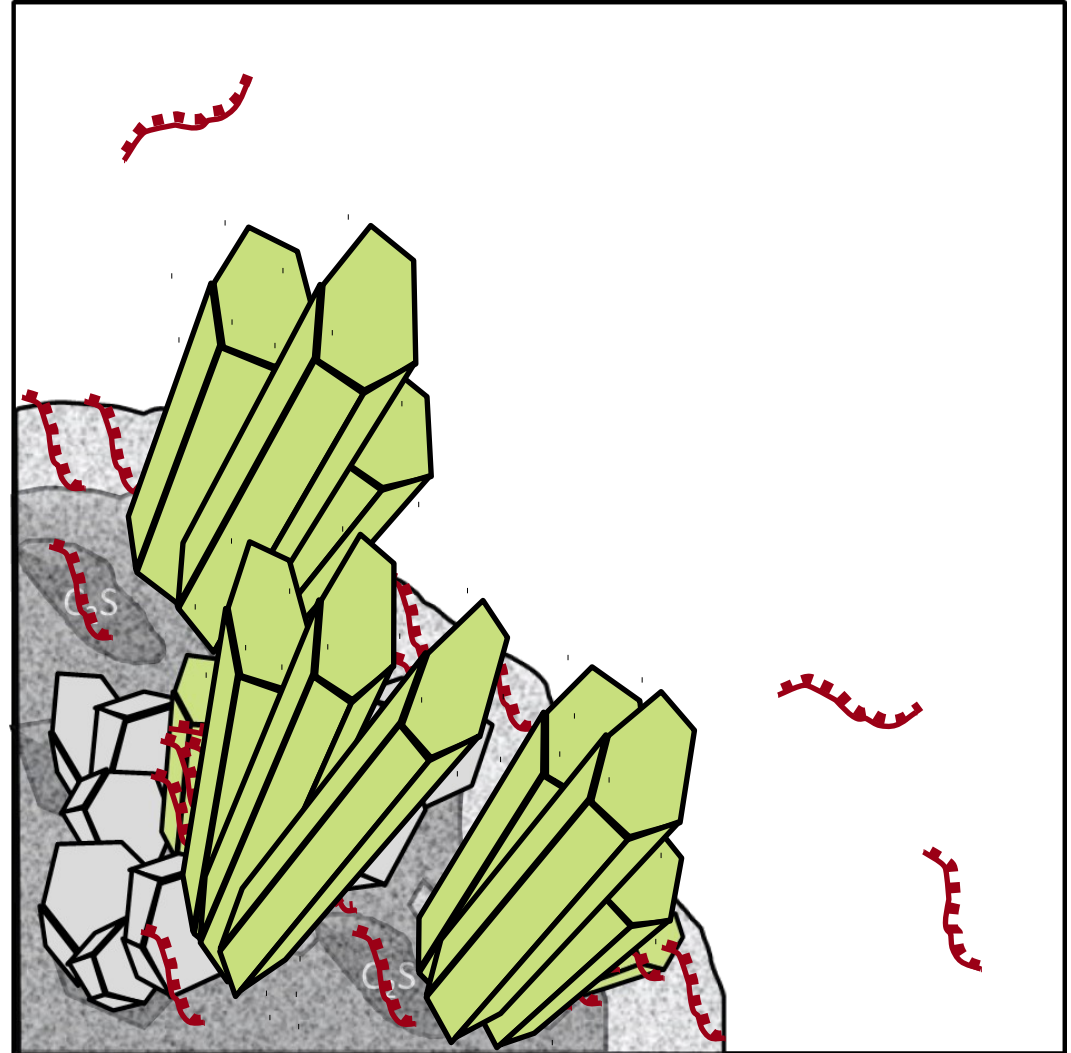


Rheology effects

Time effects

With PCE in the pore solution a number of effects occur in parallel:

- Direct adsorption
- or via counter ions
- Cross linking via Ca^{2+}
- Competitive adsorption
- Not all polymers are adsorbed immediately.
- Ongoing hydration reduces the effect of adsorbed polymers.

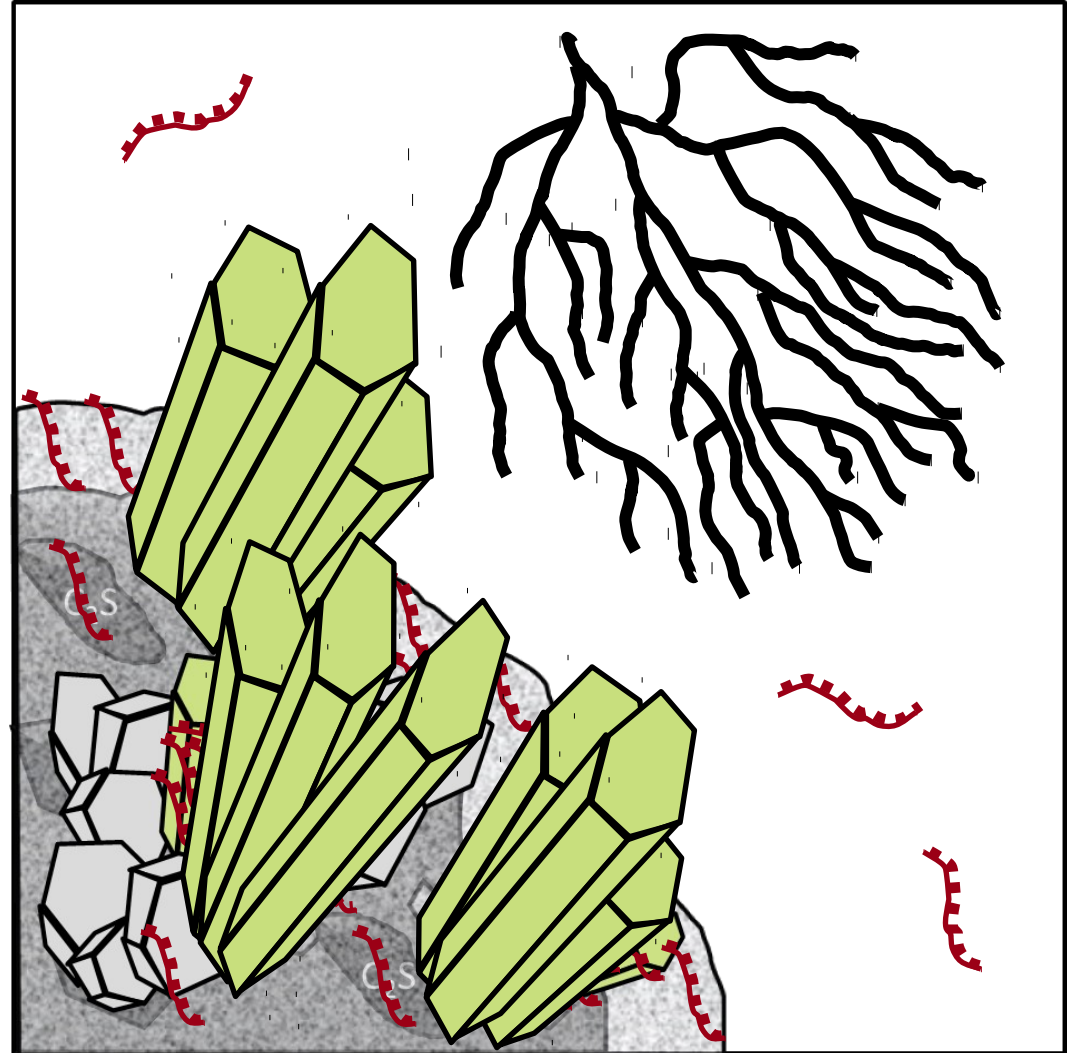


Rheology effects

Supplementary polymers

With PCE in the pore solution a number of effects occur in parallel:

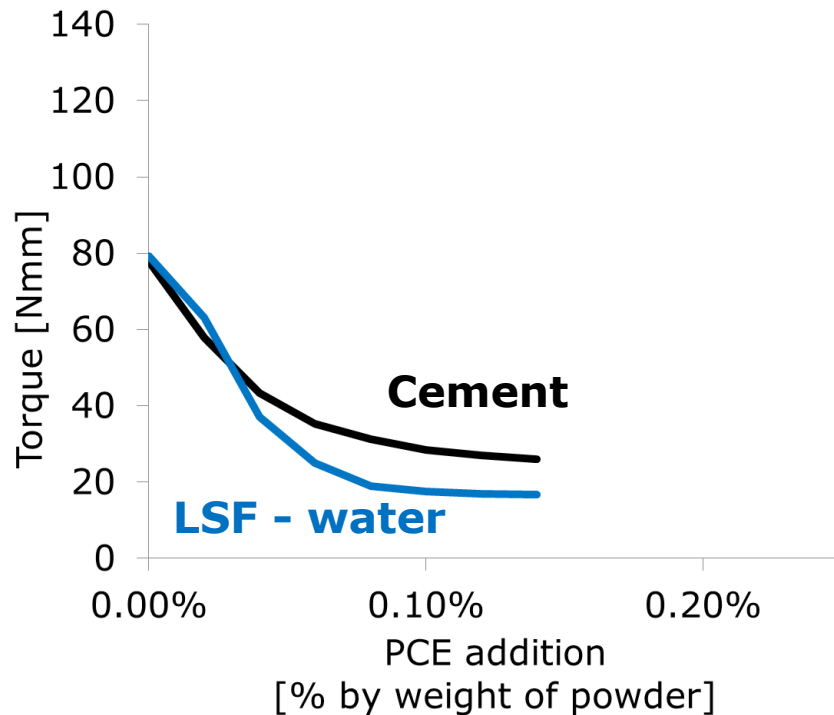
- Direct adsorption
- or via counter ions
- Cross linking via Ca^{2+}
- Competitive adsorption
- Not all polymers are adsorbed immediately.
- Ongoing hydration reduces the effect of adsorbed polymers,
- Supplementary polymers can interfere.



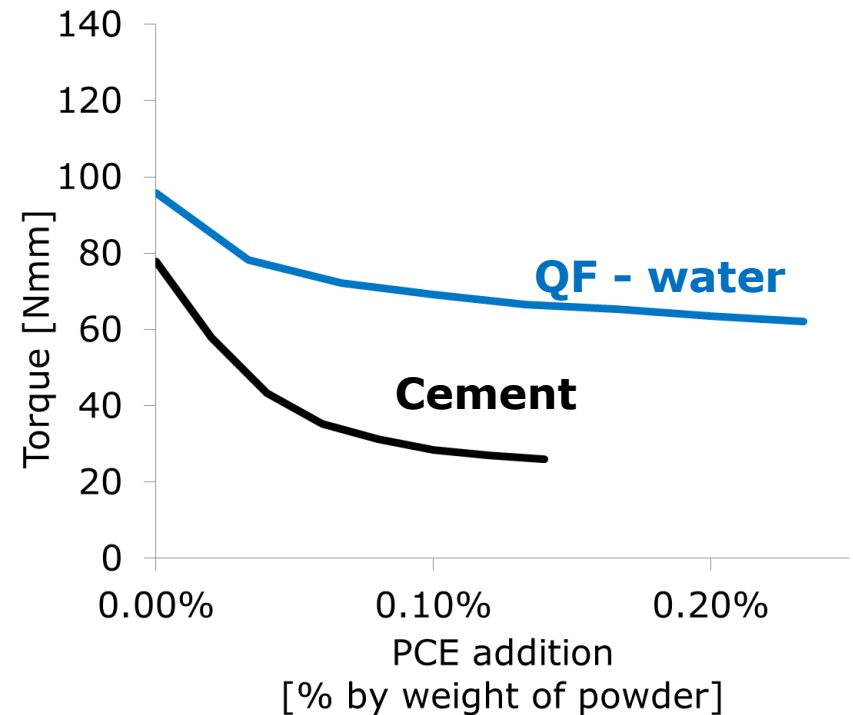
Rheology effects

Interactions with fillers

Limestone filler



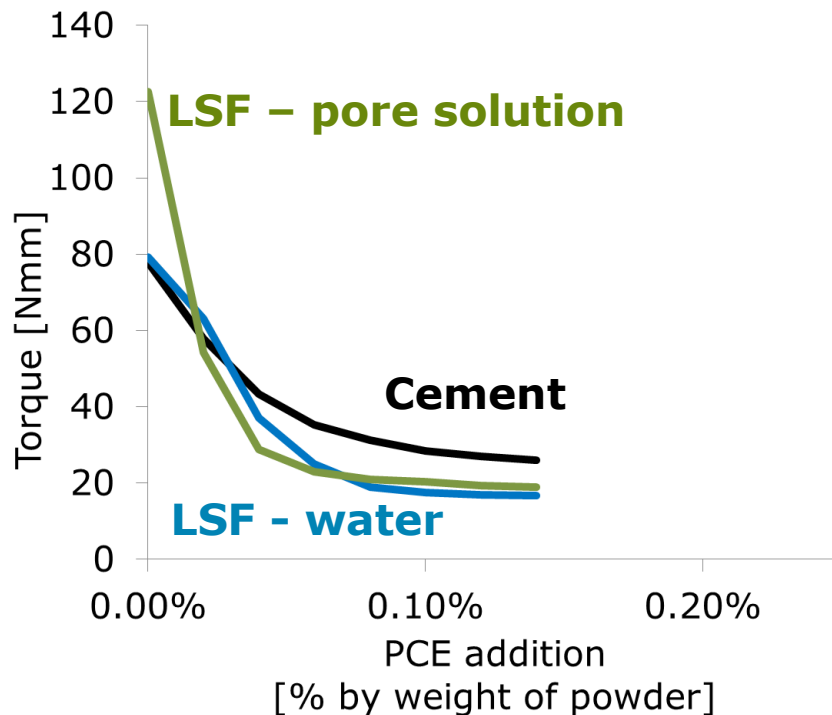
Quartz filler



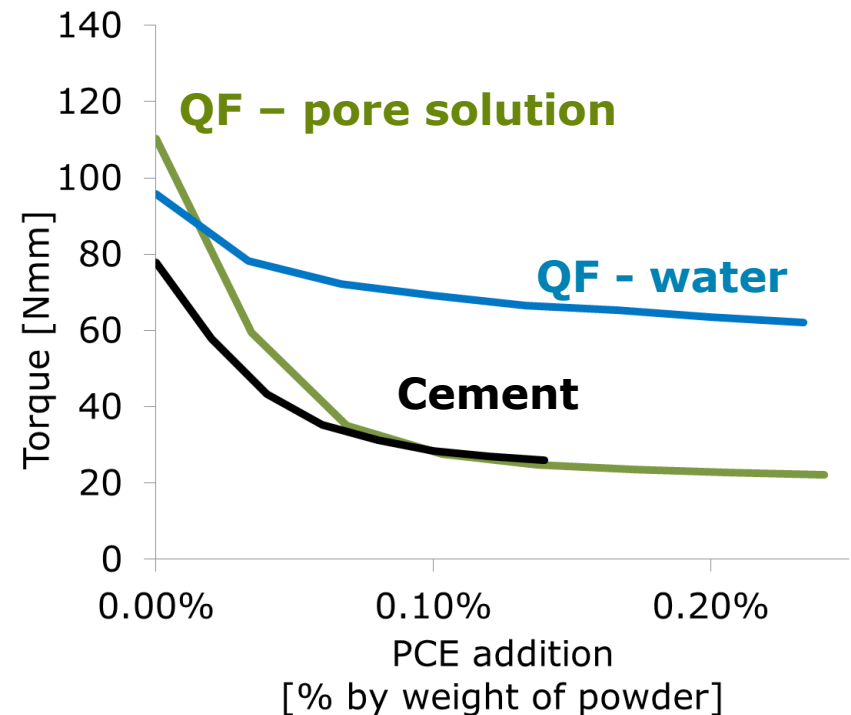
Rheology effects

Interactions with fillers

Limestone filler

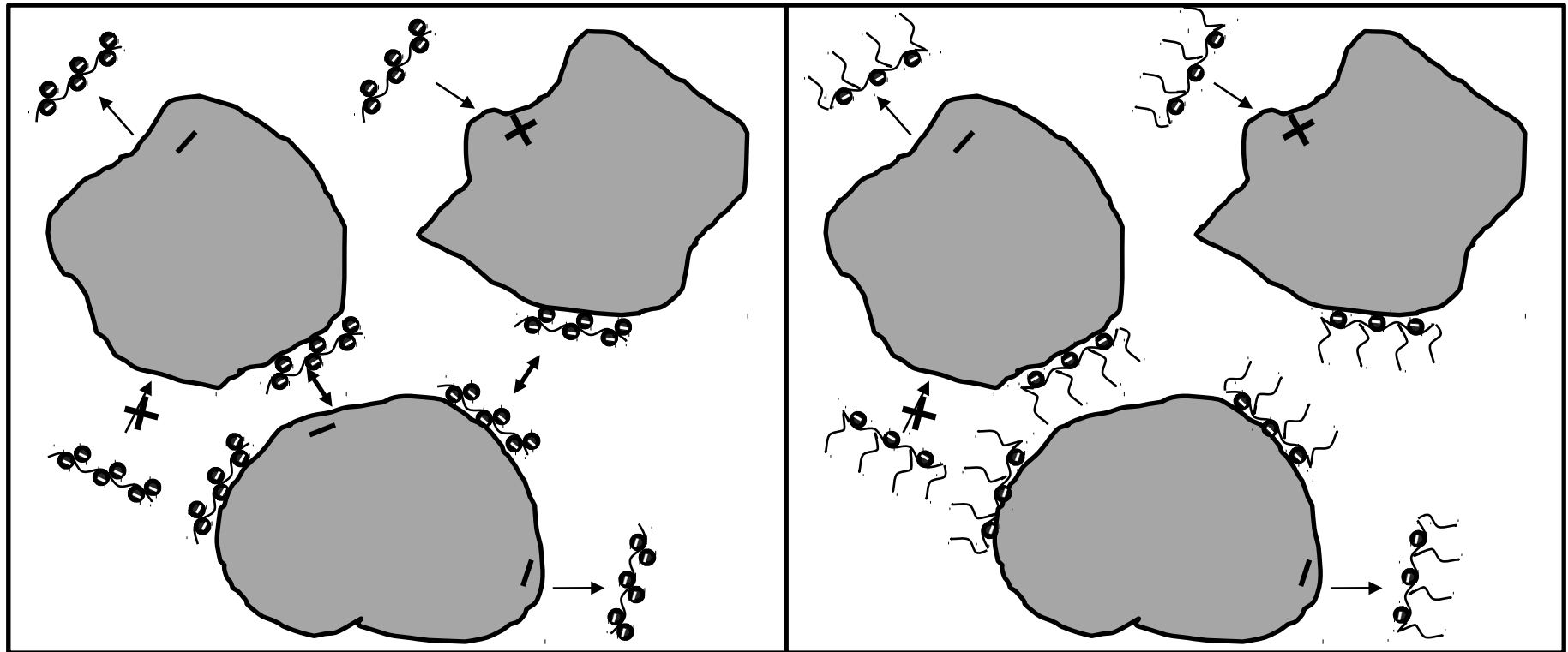


Quartz filler



Rheology effects

Dispersion mechanism after adsorption

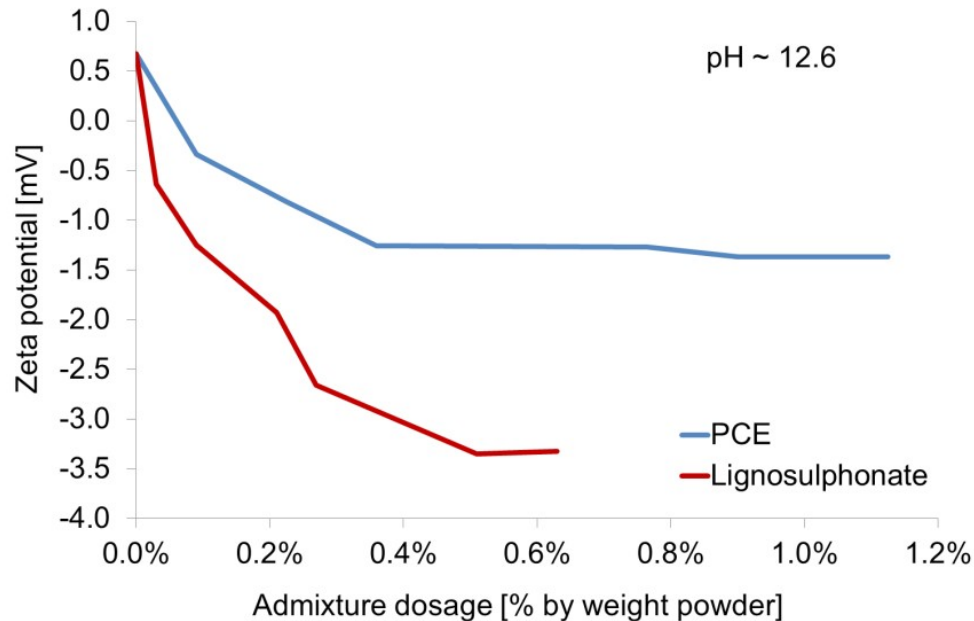


Electrostatic repulsion

Steric repulsion

Rheology effects

Dispersion mechanism after adsorption

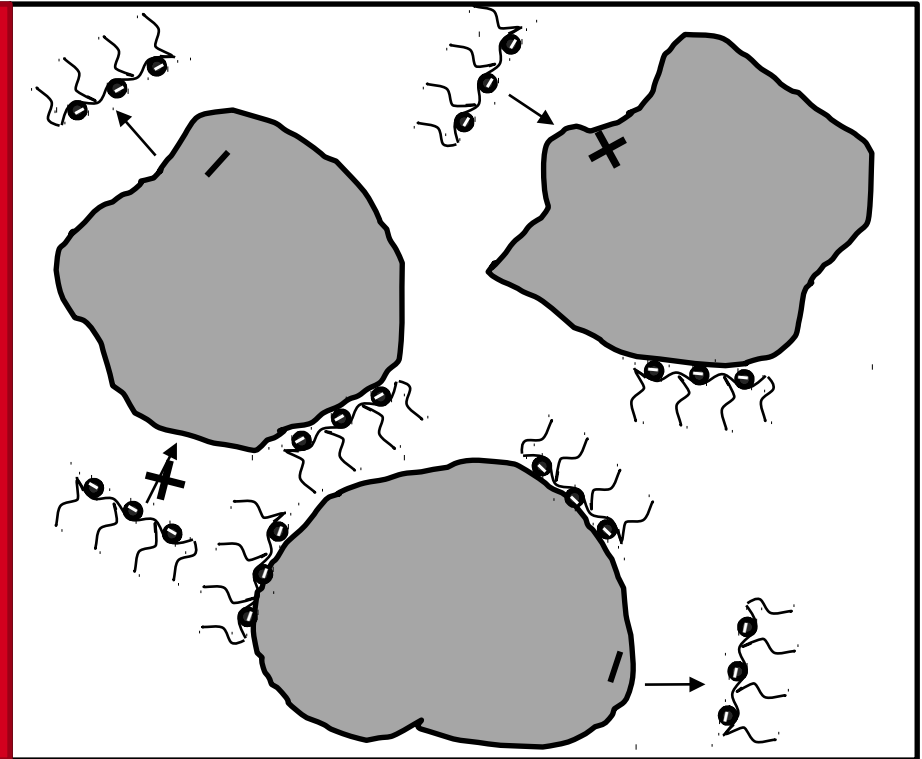


**Stability starts at zeta potentials of
> 30 mV
or
< -30 mV**

Rheology effects

Dispersion mechanism after adsorption

Assumably the steric effect is the dominating effect, regardless of the superplasticizer type.

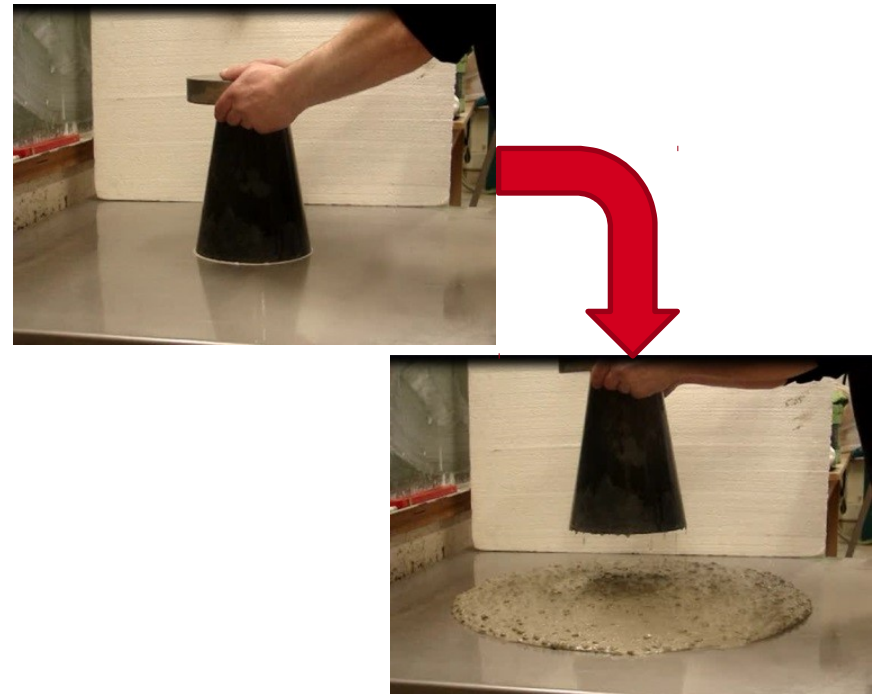
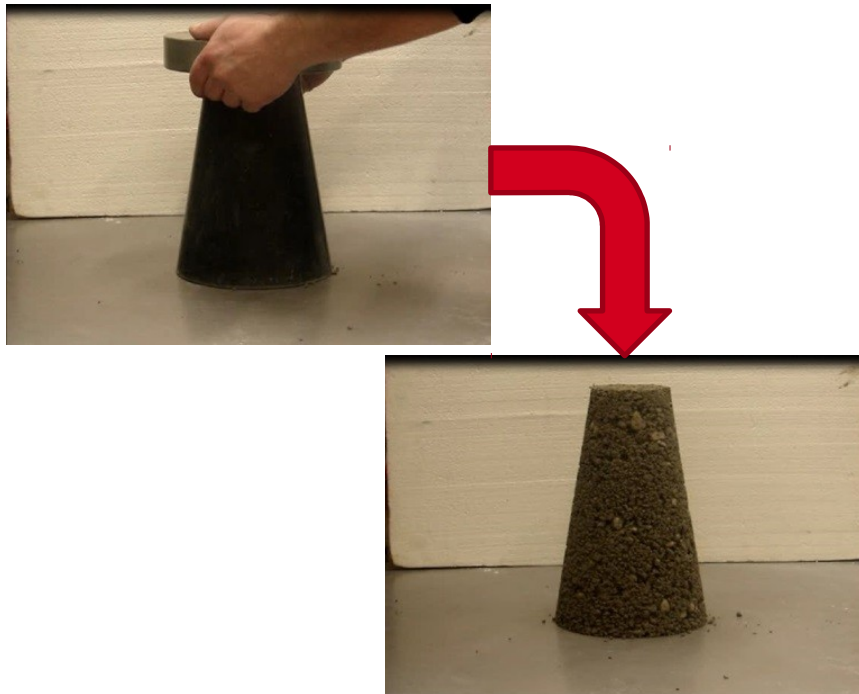


Electrostatic repulsion

Steric repulsion

Rheology effects

Dimensions



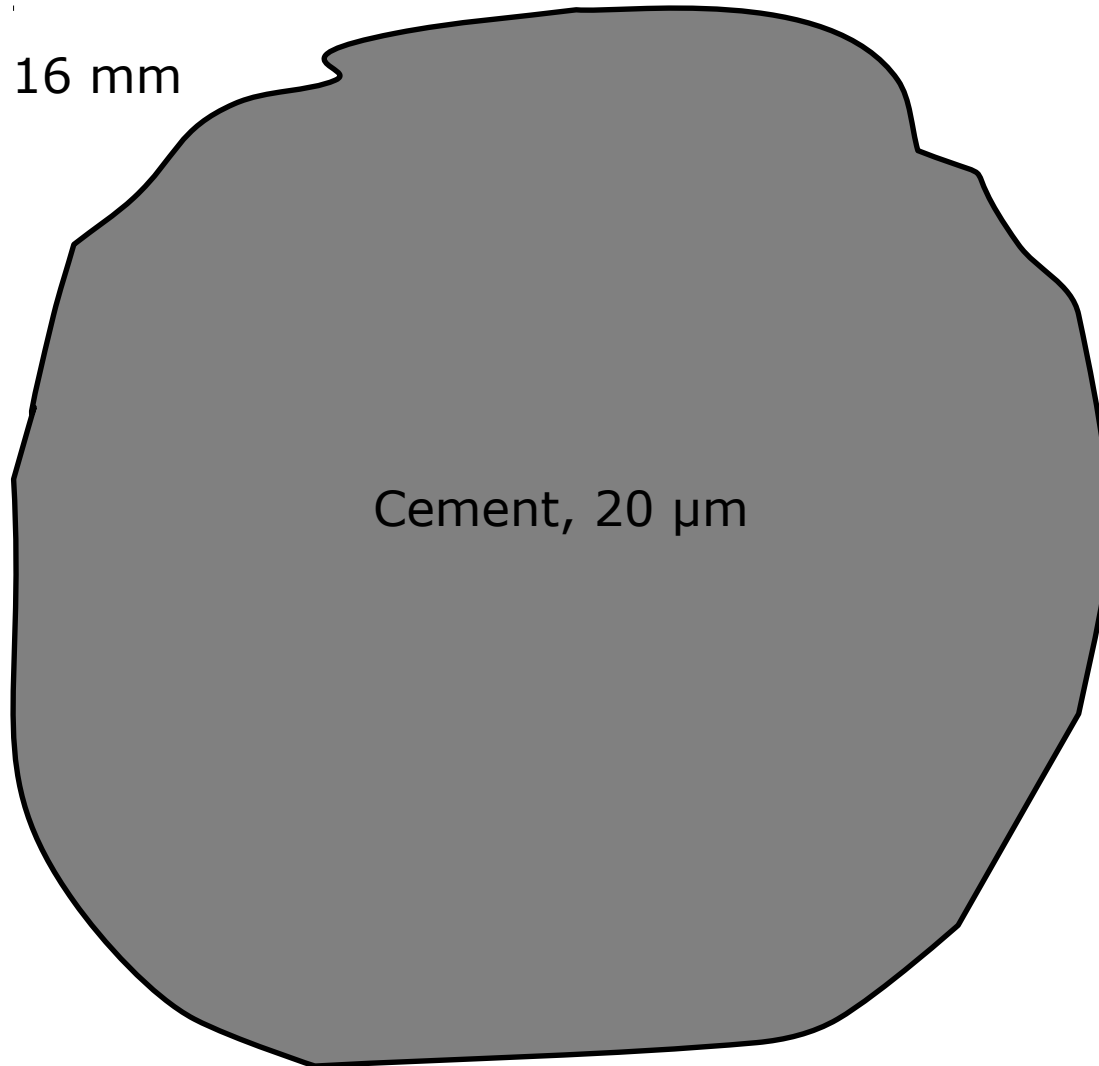
Concrete without SP.

Identical concrete with PCE
(≈ 0.7 % bwo cement, or 0.096 % bwo concrete)

Rheology effects

Dimensions

Aggregate, 16 mm



Cement, 20 μm

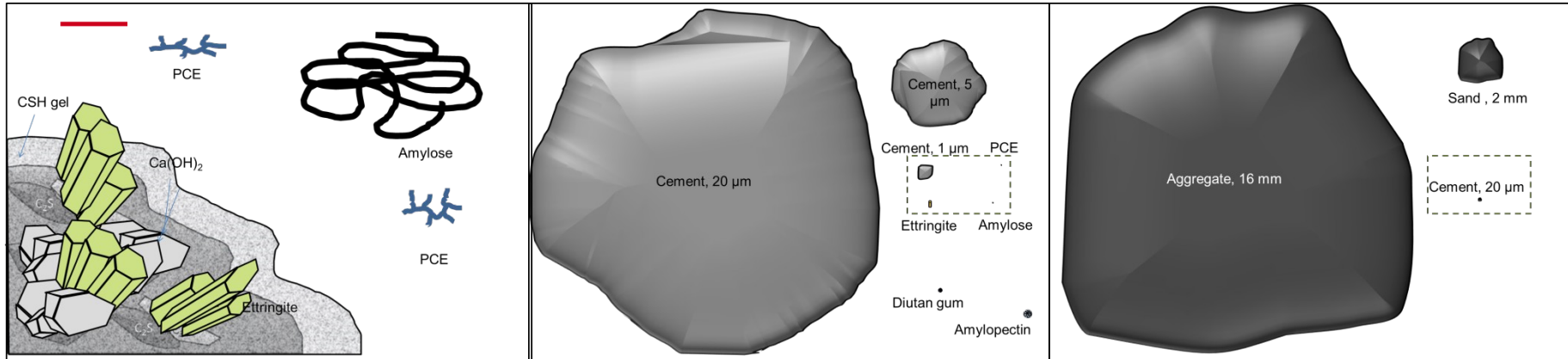

Ettringite


Amylopectin


PCE

Rheology effects

Dimensions



PCE vs.
ettringite



Wikipedia

PCE vs.
cement particle



Wikipedia

PCE vs.
aggregate

Why is it necessary to understand these effects?

High strength or 28-d strength are really not a challenge today!

Real challenges are to:

- Tailor slump life and setting
- Adjust yield stress and viscosity independently
- Make concrete more pumpable, flowable, sticky
- Modify and tailor the hydration
- Modify properties on various organic and inorganic constituents
- Cope with existing and upcoming systems including multiple component or alkaline activated binder systems

The solutions can be found on sub-micron scale!



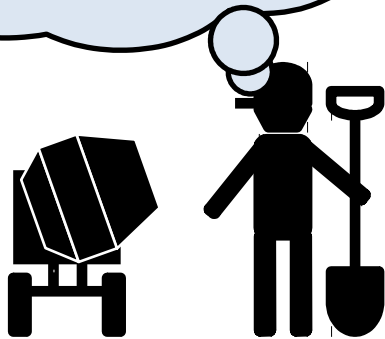
Problems implementing more knowledge based concepts into concrete technology



Problems

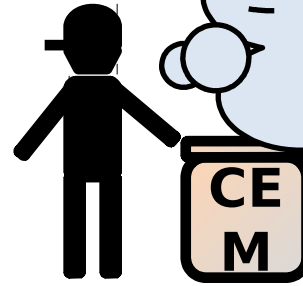
Mindset of the involved parties

Concrete exhibits a Young's modulus, compressive strength and the w/c is of importance



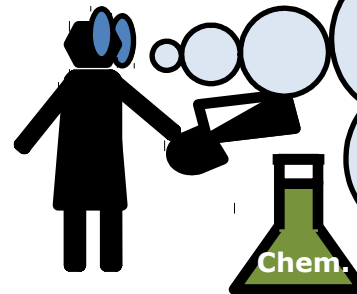
Construction engineers

Let us keep the temperature and Blaine value stable.



Cement producers

What is so different between a construction site and a chemical laboratory?

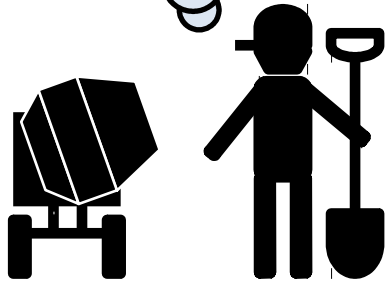


Construction chemistry

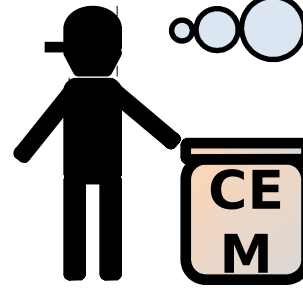
Problems

Who is to blame?

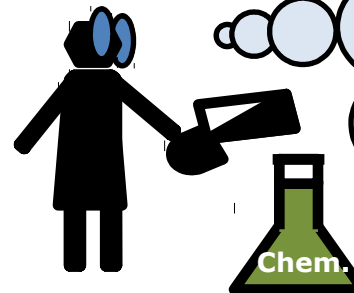
New cement types are evil!
Admixtures are witchcraft!



Construction engineers



Cement producers



Construction chemistry

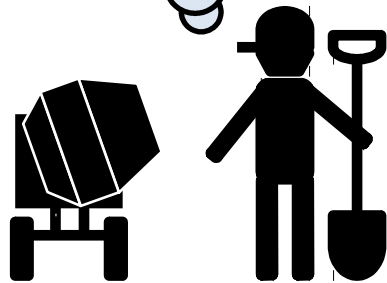
Cements fulfil the standard. The construction chemical industry has to provide more stable products.

Too much cement quality scatter. Nevertheless, we provide a tailored admixture for every cement type.

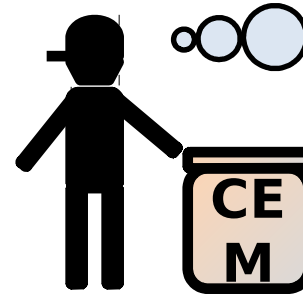
Problems

Who is right?

Refusing new cement types and construction chemicals is backward. Engineers have to become more flexible and have to learn new competences.



Construction engineers



Cement producers



Construction chemistry

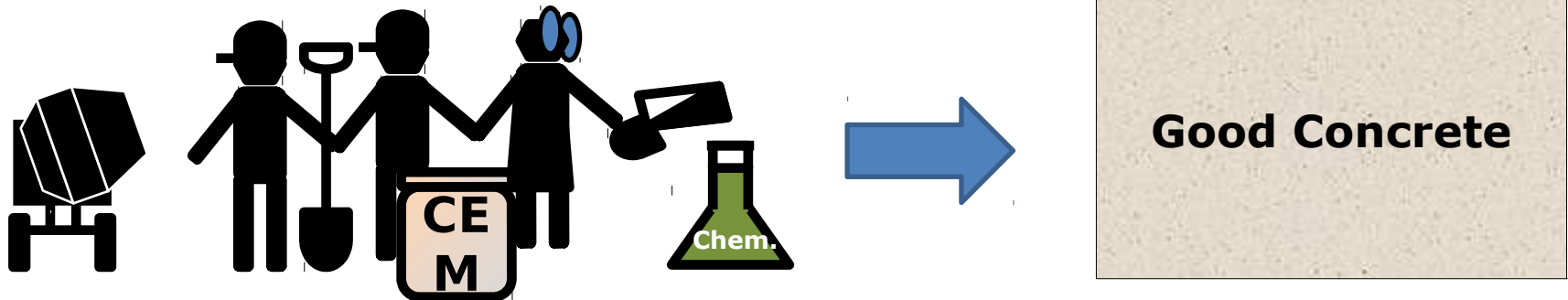
Not a single specification in cement standards provides information about interactions with superplasticizers!

Tailored PCEs fail, if the boundary framework changes! It would be more important to train users more adequately.

Problems

Who is right?

- Cement – the most important binder material – can impossibly be produced in a constant quality as would desirable for superplasticizers.
- In order to use SP efficiently, influences from the entire concrete system have to be considered.
- Superplasticizer can improve a lot, but it is not a marvel that can absorb poor concrete design.



- **Good concrete can only be designed based on a multi-disciplinary basis.**



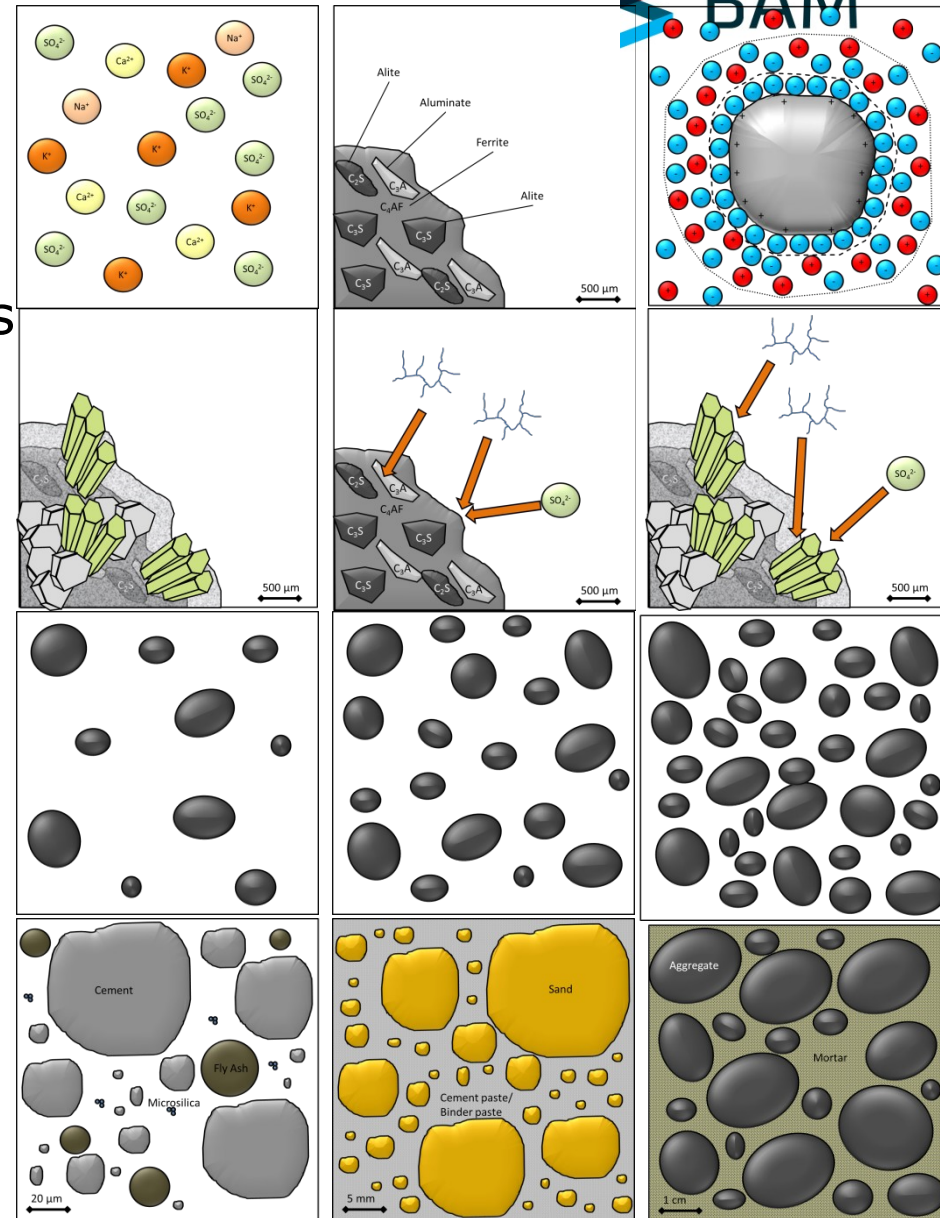
Conclusions



Conclusions

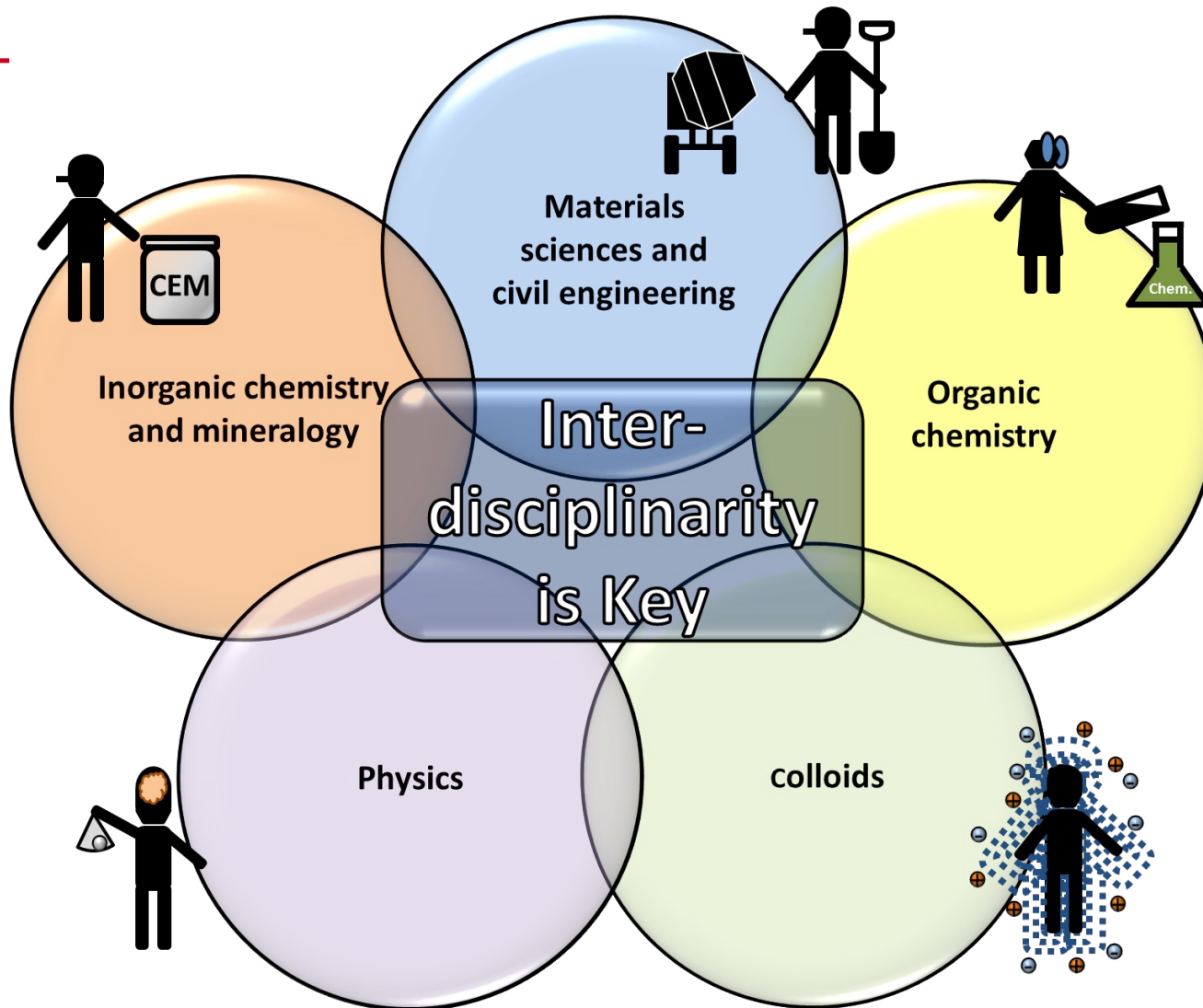
Influencing factors

- Ion content and strength
- Surface chemistry and charges
- Morphology
- Hydration phases
- Polymer sizes and structure
- Selective adsorption
- Competitive adsorption
- Different particle charges
- Different particle sizes
- Solid volume fraction
- PSD of finest particles
- PSD of coarser particles
- Interaction of particle sizes



Conclusions

Skills required



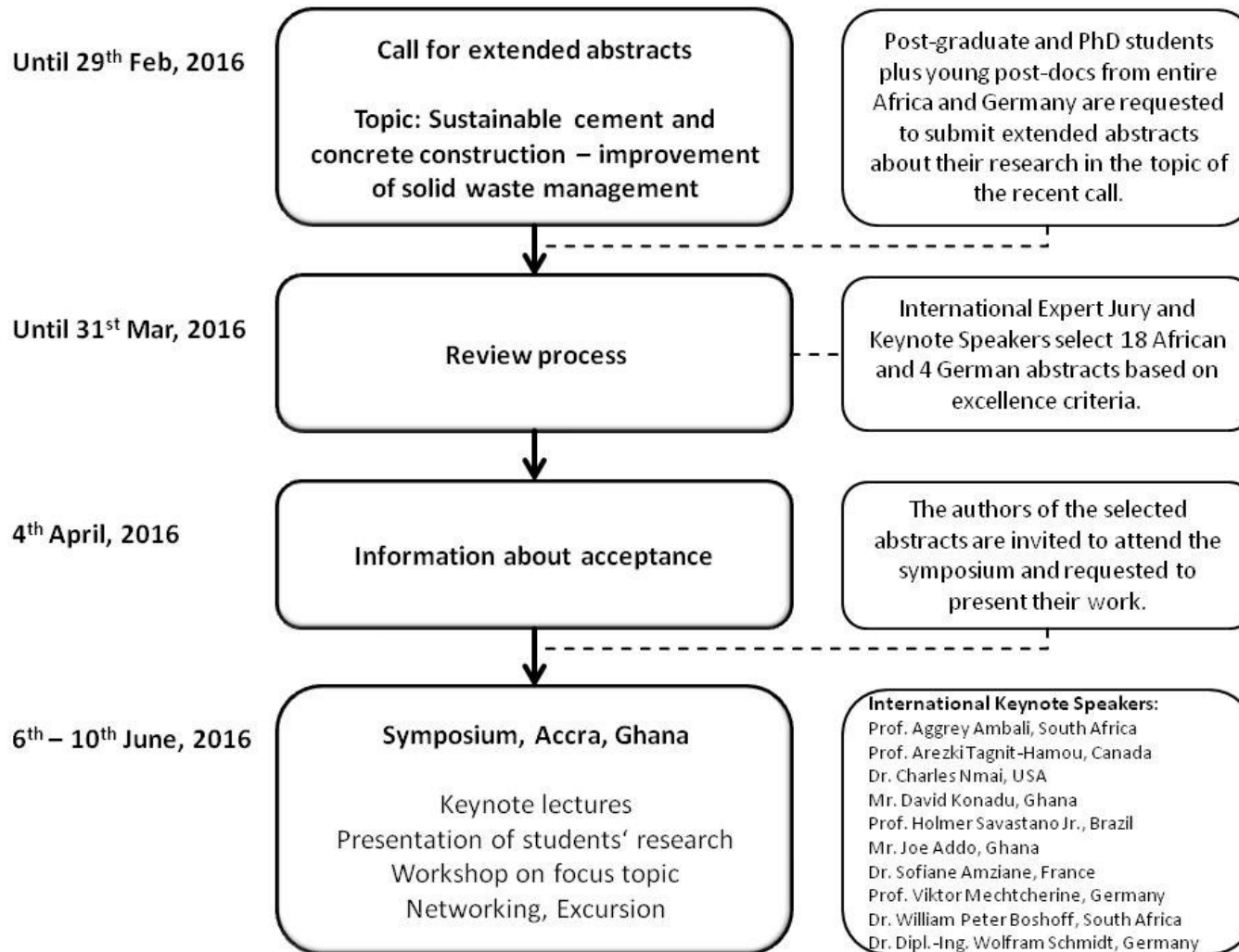
Way forward

- For sustainable and future oriented concrete we have to change our mindset! Let us not be „chicken to change“!
- Rheology is key! Poor workability compromises long term performance and durability.
- Macroscopic flow phenomena typically have their origin on much smaller size (up to 10^7 times smaller)
- In order to understand and successfully apply modern concrete types, new skills are required for civil engineers that include awareness physico-chemical processes.

Thank you very much for your kind attention!

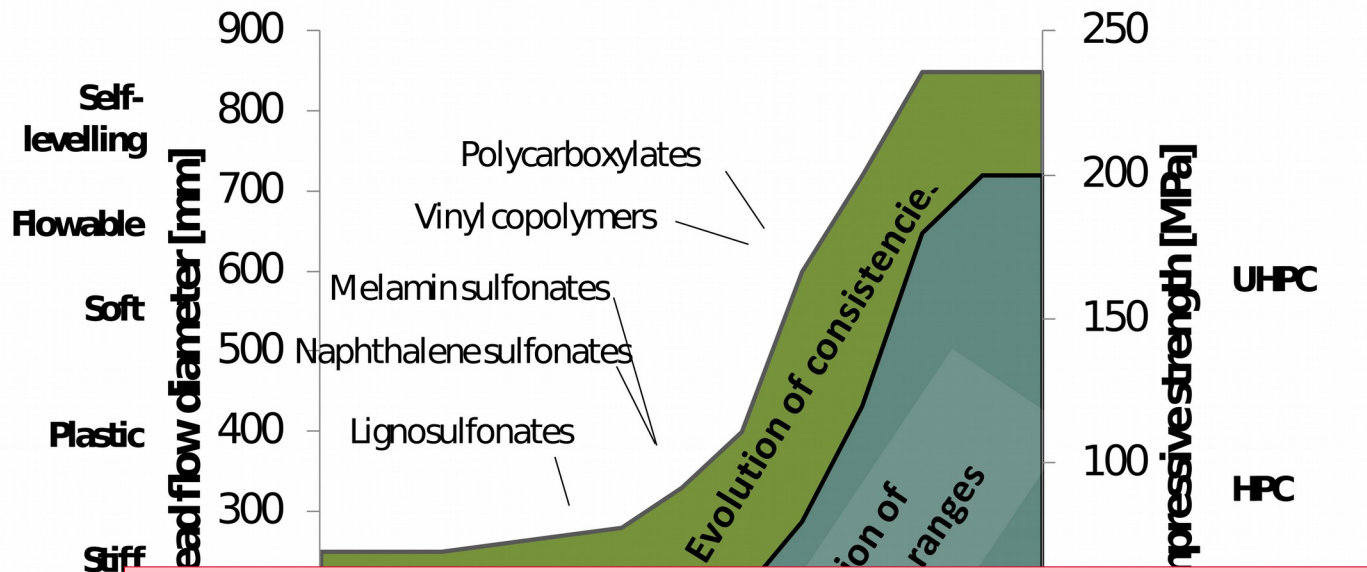
**For further information:
Visit: www.bam.de [≡] M-Flow Project**

Announcement – KEYS



Introduction

Rheology modifying admixtures



Rheology modifying admixtures are the key to better performance.

Unfortunately their mode of operation is complex!