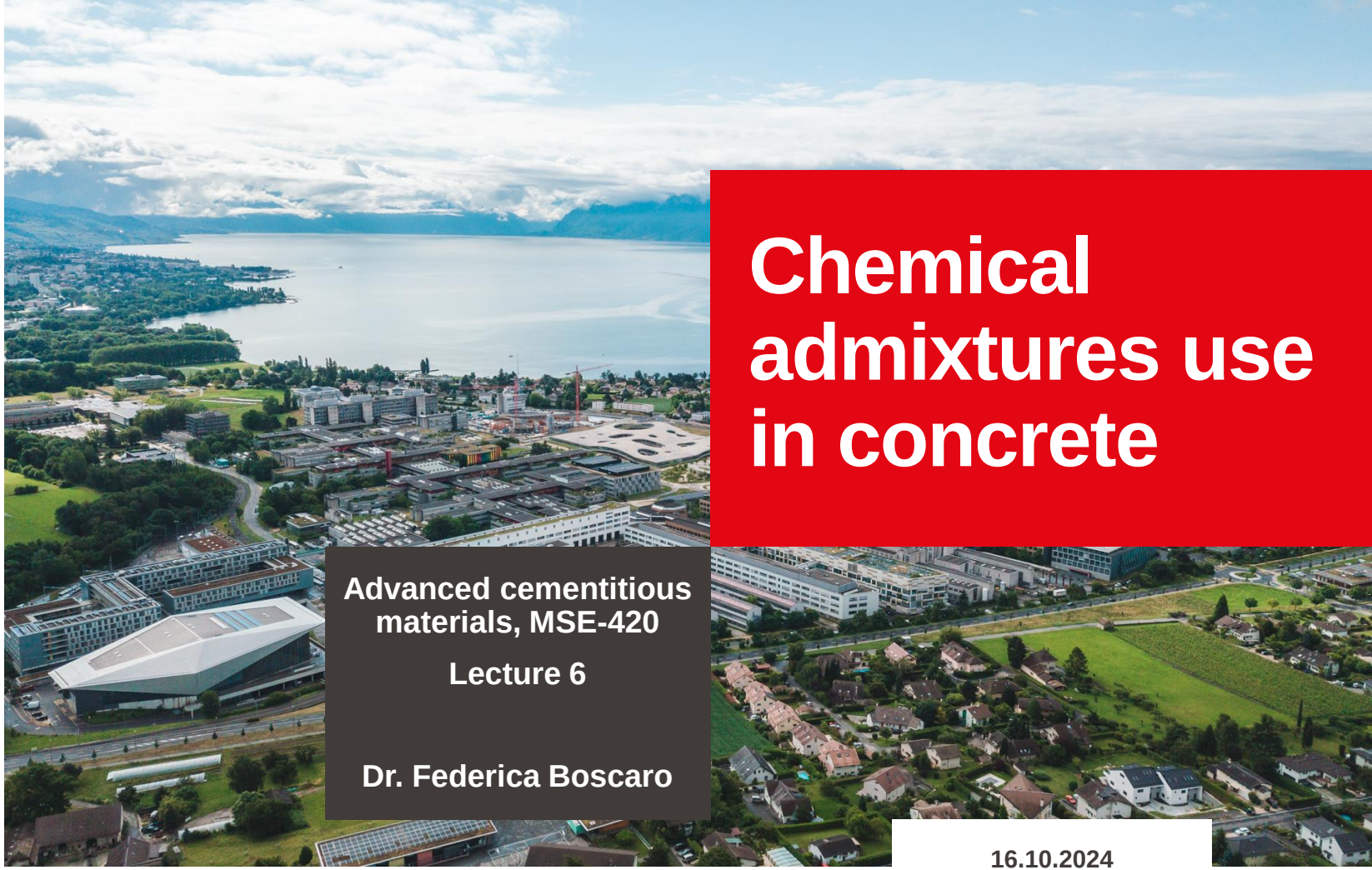
EPFL

LABORATORY OF CONSTRUCTION MATERIALS



Chemical admixtures use in concrete

Advanced cementitious materials, MSE-420

Lecture 6

Dr. Federica Boscaro

16.10.2024

Learning objectives

By the end of this class, you will be able to...

- **Identify** the main chemical admixtures in concrete technology
- **Describe** their effect on cement and concrete properties, their mechanism of action and their interactions with other chemical admixtures
- **Suggest** what admixture(s) shall be used in a specific application, taking into account environmental conditions
- **Relate** the use of chemical admixtures to environmentally friendly concrete and sustainability

Chemical admixtures

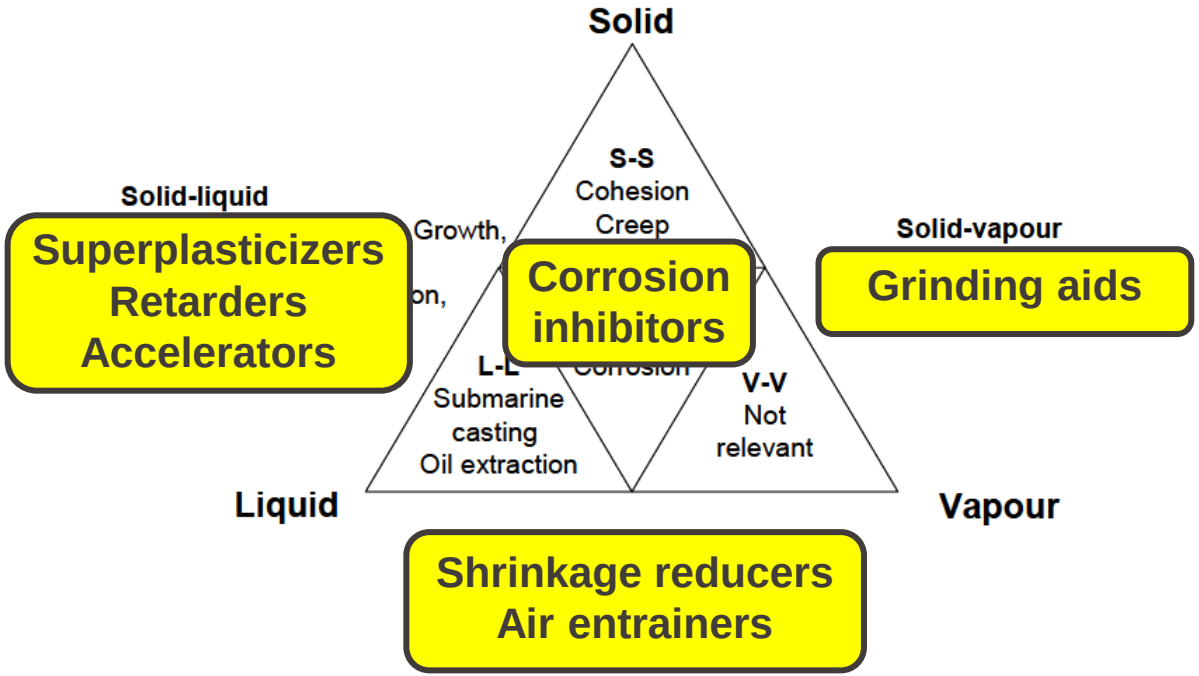
- **Dosage**
  - In small amounts and in the right proportions, they can radically change essential properties of the mix
  - In too small amounts: they will go unnoticed
  - In too large amounts: they may lead to undesired effects

  - More powerful the admixtures are, less amounts are needed, BUT it becomes easier to overdose them

- **Blends**
  - Admixtures may be blended before use and supplied as blended. This simplifies specific applications, but they cannot be used for everything everywhere.

Interfaces in concrete

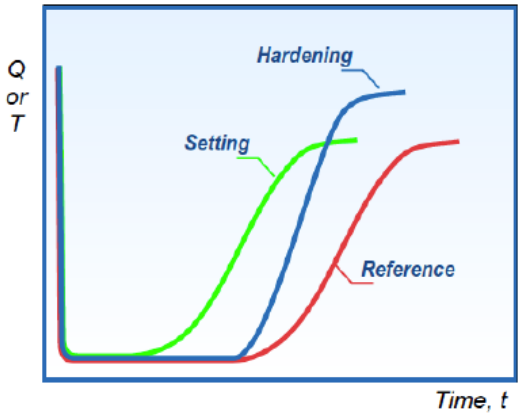
Admixtures act at the interfaces, reason why they have such strong effects at very low dosages



Flatt et al., Journal of the European Ceramic Society, 32, 11, 2012

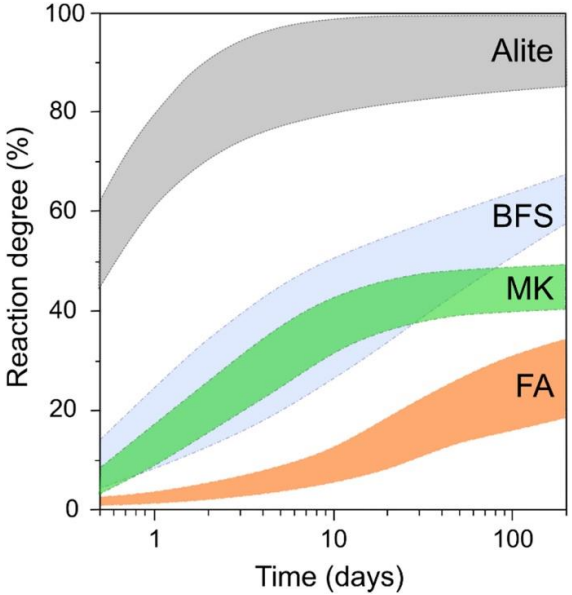
Accelerators

- Widely used to **reduce the setting time, boost cement hydration or enhance the performance of blended cements**
- Allow rapid repair of surfaces, reduce the curing time, compensate for low temperature climates
- Most common accelerators: Soluble inorganic salts and organic compounds
- Diverse mode of action, physical or chemical effect
- Division in classes depending on their effect:
  - **Set accelerators**:
    - Reduce setting time of concrete
    - Silicate and aluminate salts
  - **Hardening accelerators**:
    - Increase the early strength of concrete
    - $CaCl_2$ (also set accelerator), etc.

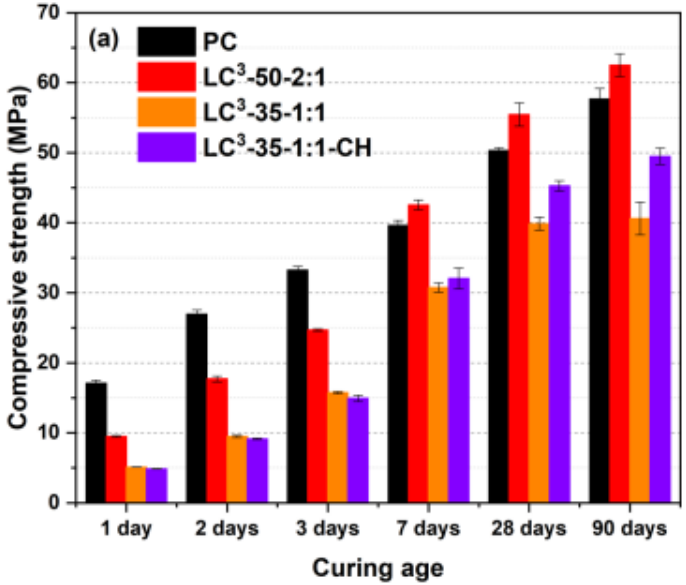


Myrdal, 2007

Accelerators and blended cements



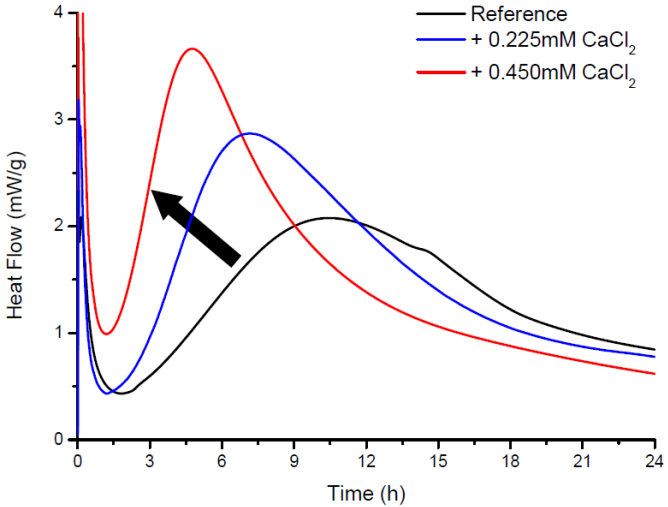
Skibsted & Snellings, Cement and Concrete Research, 124, 2019



Zunino et al., 2023

Accelerators – Calcium Chloride

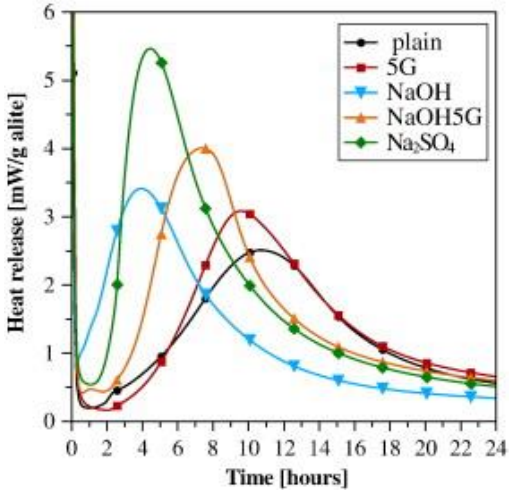
- Most efficient accelerator
- Used in concrete since 1873 (patent in 1885)
- Use in concrete is permitted with restrictions or prohibited
- Mode of action not completely understood (probably it deals both with nucleation and dissolution kinetics)

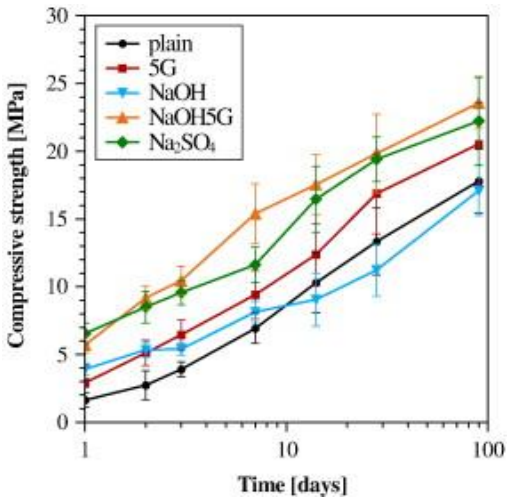


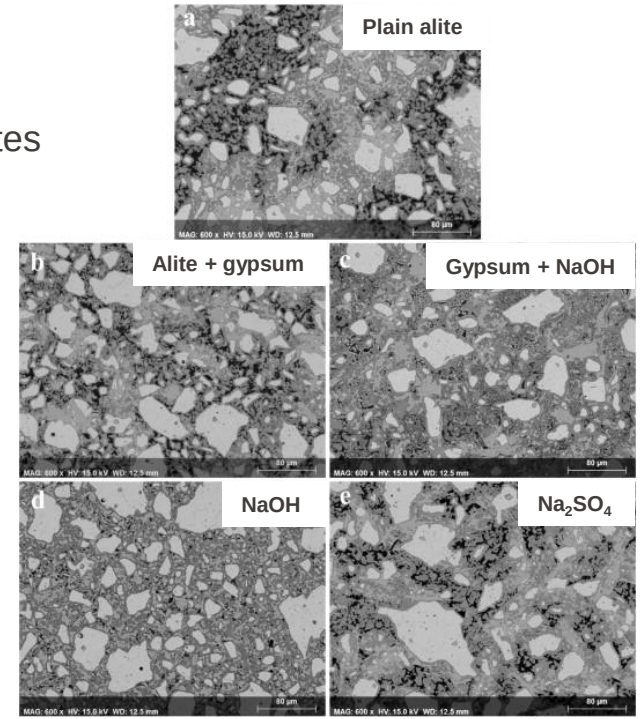
Courtesy of Dr. P Juilland (Sika AG)

Accelerators – Alkali and sulfate

- Early acceleration of alite hydration rate
- Negative impact on long-term strength
  - Lack of consensus on the mechanism behind this decrease
  - Differences in the morphology and composition of the hydrates (C-S-H, CH)



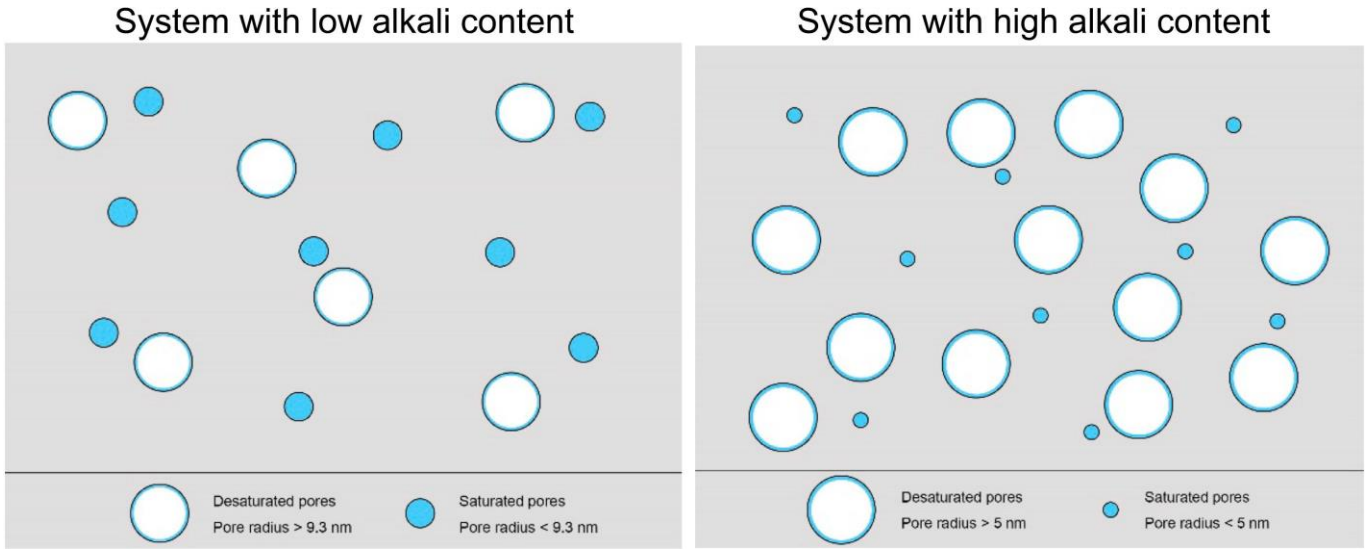




Mota et al, Cement and Concrete Research, 75, 2015

Accelerators – Alkali

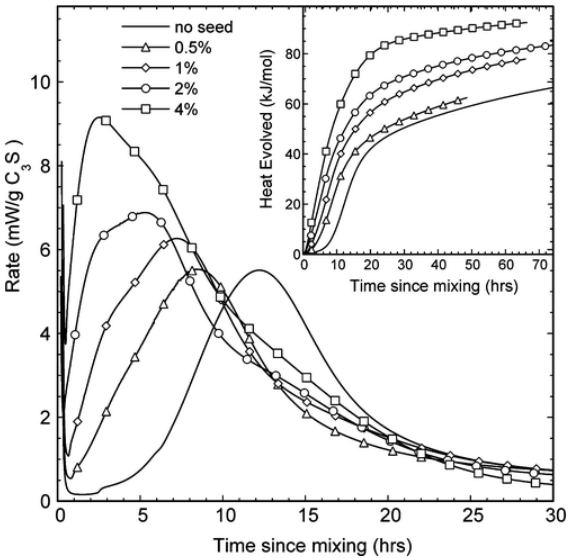
- Higher and faster drop in internal RH, faster desaturation of the larger pores, further hydrate growth is limited
- Saturated small pores, higher supersaturation needed, slow down of the hydration rate, lower DoH

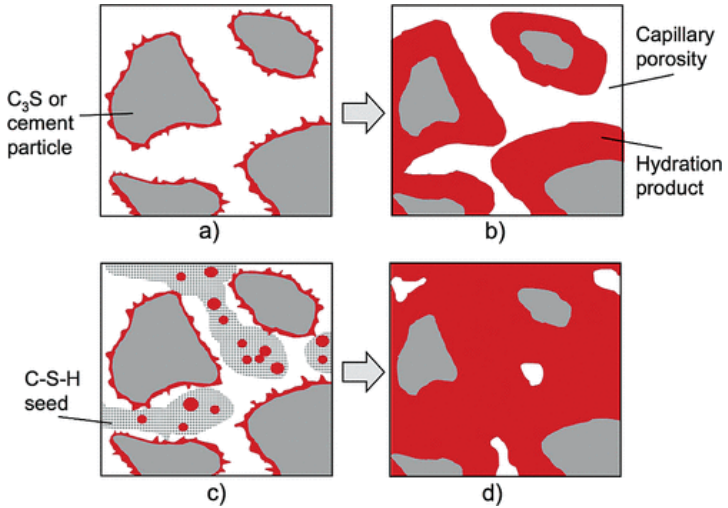


Zhang et al., Cement and Concrete Research, 174,2023

Accelerators – Seeding approach (C-S-H nuclei)

- Physical effect: increasing of surfaces availability for hydrates precipitation
- Reduction of capillary porosity, more homogeneous distribution of C-S-H in comparison to plain C_3S



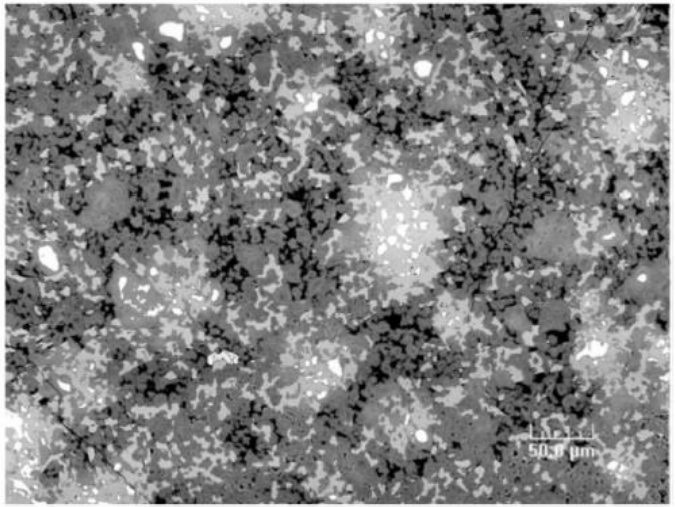


Thomas et al, The Journal of Physical Chemistry C, 113, 11, 2009

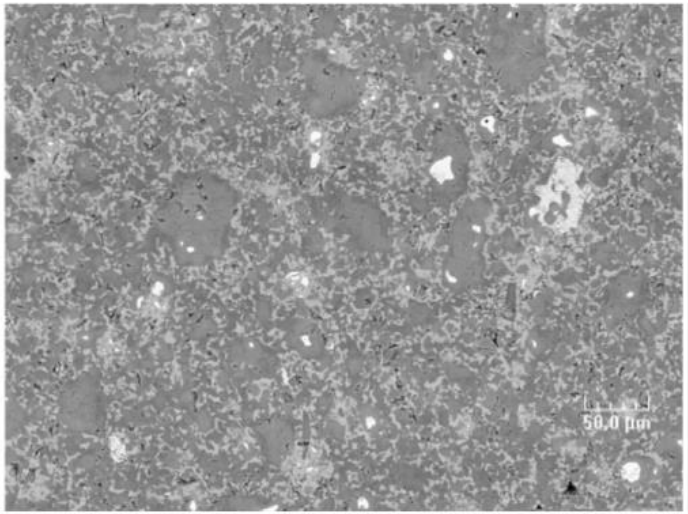
Accelerators – Seeding approach (C-S-H nuclei)

Microstructure after 28 days

Without C-S-H seed



2% C-S-H seed



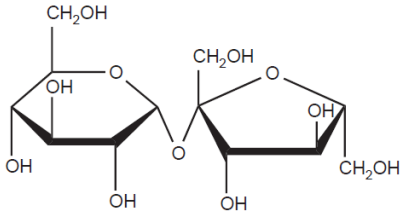
Thomas et al, The Journal of Physical Chemistry C, 113, 11, 2009

Retarders

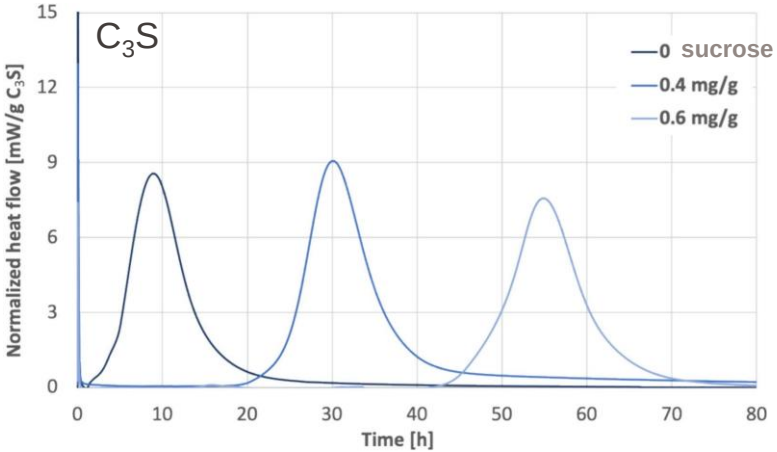
- When **delay of the initial setting time** of concrete is needed
- Type of retarders: lignosulfonates, some salts of carboxylic acid, sugars or sugar derivatives, some inorganic salts
- Many retarders also have a water-reducing action, and many water-reducers retard cement hydration
- Sugars are used as cement hydration retarders: **Sucrose** is the most effective one

Nonretarding	Good retarders	Excellent retarders
α-Methyl glucoside[b] Thehalose[b]	Glucose[a] Maltose[a] Lactose[a] Cellobiose[a]	Sucrose[b] Raffinose[b]

Thomas & Birchall, 1983



Retarders – Sucrose



Xu et al, Cement and Concrete Research, 181, 2024

Shift of the acceleration period to later times

Retarders – Sucrose

Mechanisms of retardation

Still a matter of debate:

- Complexation of calcium ions
- Hindering of the nucleation and growth of hydrates
- Hindering of the dissolution of anhydrous phases
- Perturbation of the aluminate-silicate-sulfate balance

Retarders – Sucrose

Mechanisms of retardation

1. Retardation is impacted by adsorption
2. Limited impact of sucrose on C-S-H precipitation
3. Addition of CH to a cement paste retarded with sucrose reduces retardation proportionally to the total surface area of CH
4. Nucleation and growth of CH is affected by sucrose at pH from 12.5 to 13.2
5. Rate of hydration at the induction period is proportional to the free C_3S surface -> indirect demonstration that sucrose adsorption hinders C_3S dissolution (pH 13).

Similar effect in OPC when in low dosages (no significant impact on the aluminates). At higher dosages, it is more complex.

Nalet & Nonat, 2016; Reiter et al, 2015; Juilland & Gallucci, 2018; Xu et al, 2024

Dispersants (superplasticizers – SPs)

- Also called high-range water-reducing admixtures

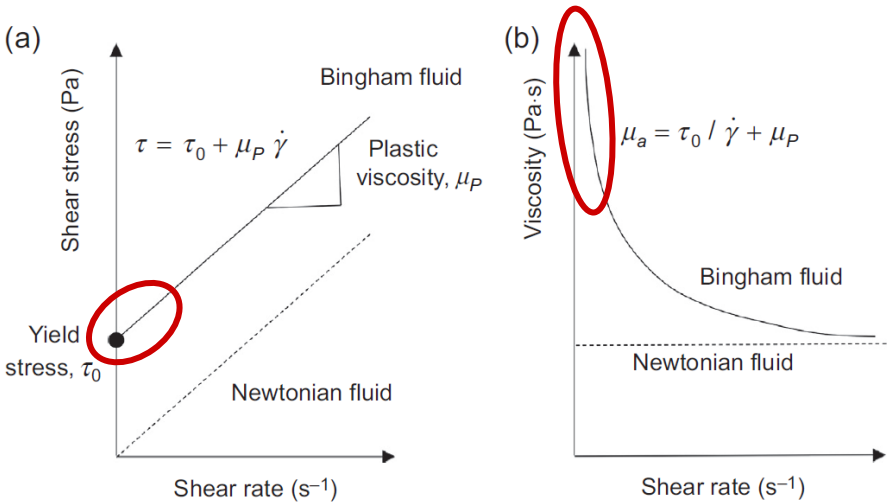
- Most common SPs among synthetic linear polymers:
  - Polynaphthalene sulphonates (PNS)
  - Polymelamine sulphonates (PMS)
  - Vinyl copolymers

- New generation of SPs: **Comb-shaped copolymers** (1980s)
  - “More effective” steric admixtures
  - Allow very low w/c ratios (0.2 or less)

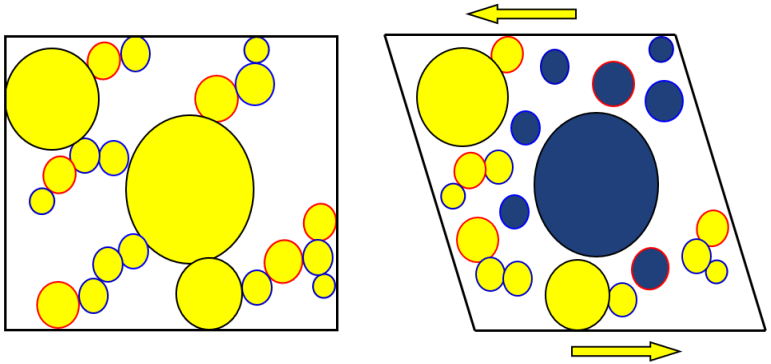
- Modify the rheological behaviour of fresh concrete

Concrete rheology

The yield stress can be viewed as a solid-liquid phase transition that takes place if enough interparticle bonds can be broken for the system to flow



Yahia et al., 2016

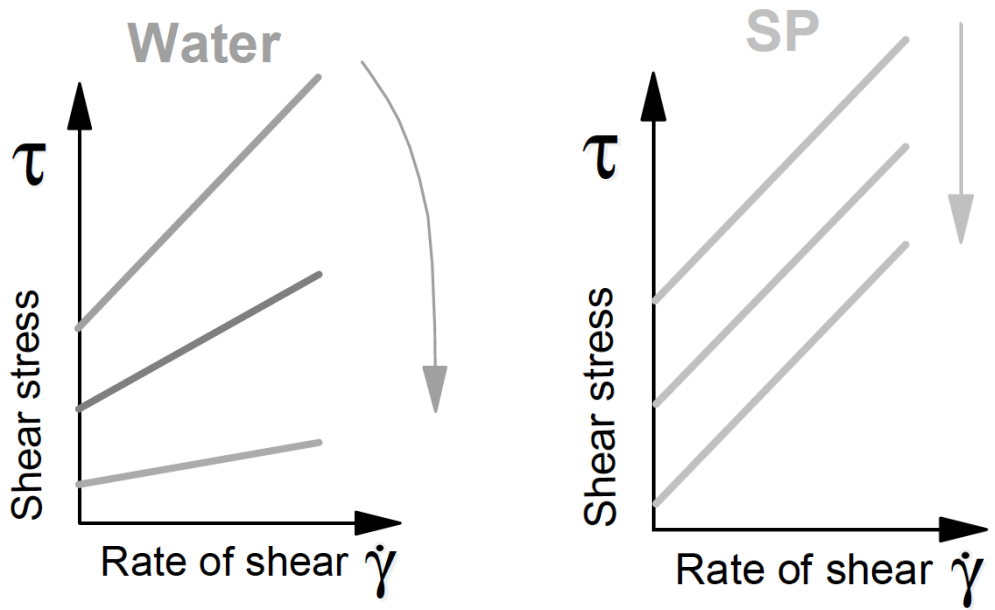


Courtesy of Prof. Flatt (ETHZ)

Concrete rheology and Superplasticizers

Changes in the mix design of concrete will impact the rheological properties, especially water

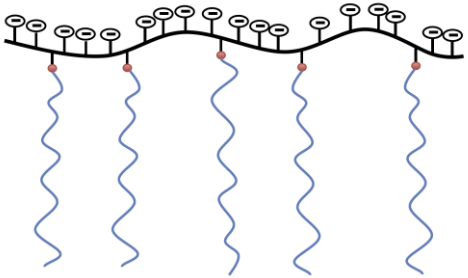
Water affects both the yield stress and plastic viscosity
SP decreases the yield stress, but barely affects the plastic viscosity



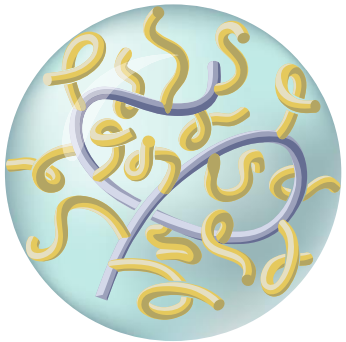
Wallevik, 2020

Polycarboxylate ethers (PCEs)

- Comb-shaped copolymers composed of a **backbone** (bearing carboxylic groups) onto which non-ionic **side chains** (polyethers) are grafted
- One of the most used admixtures in concrete technology



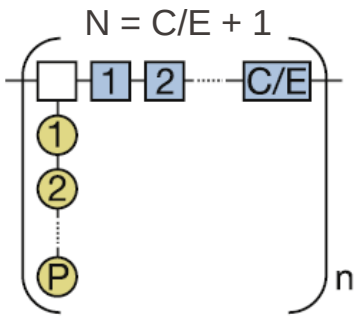
Gelardi et al., 2016



Dr. Gelardi, PhD thesis, ETHZ 2017

Main advantage of PCEs

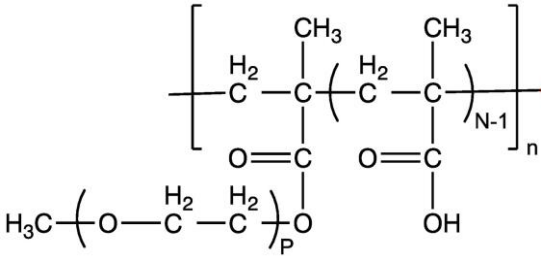
Wide range of molecular structures



- Number of repeat units
- Side chains length
- Side chains spacing
- Chemistry of side chains (limited)
- Chemistry of the backbone
  - Ionic groups (carboxylate, sulfonate, phosponate)
  - Ionic groups per monomer
  - Grafting function

Most common PCEs used in concrete have PAA or PMA backbone and MPEG side chains

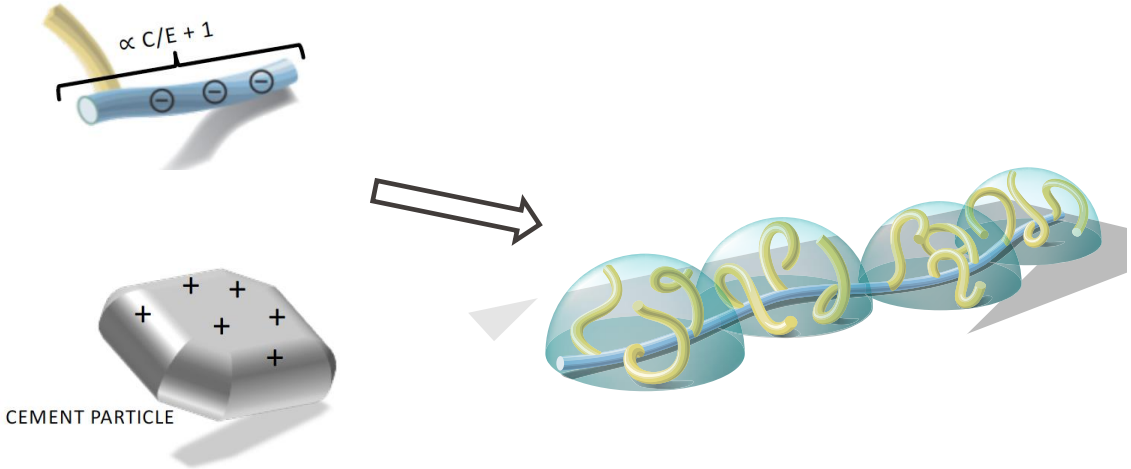
Polymethacrylic (PMA) or polyacrylic acid (PAA)



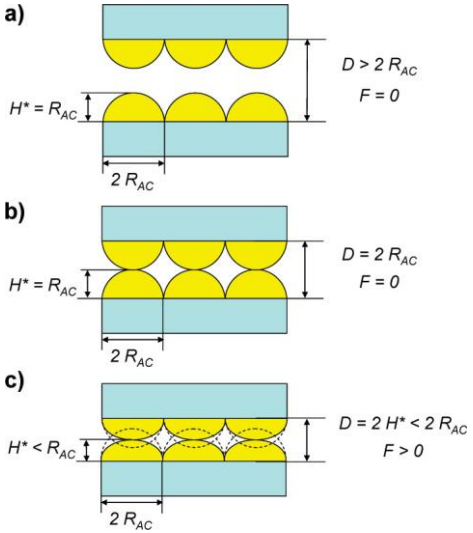
Methoxy-polyethylene glycol

Working mechanism

- The negatively charged PCE backbone adsorbs onto cement particles
- The dispersion is due to the steric hindrance induced by the side chains



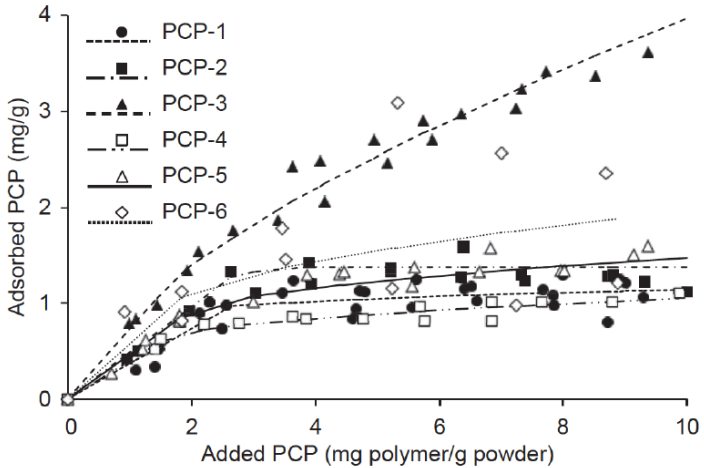
Marchon et al, Journal of the American Ceramic Society, 100, 2017



Flatt et al, Langmuir, 25, 2, 2009

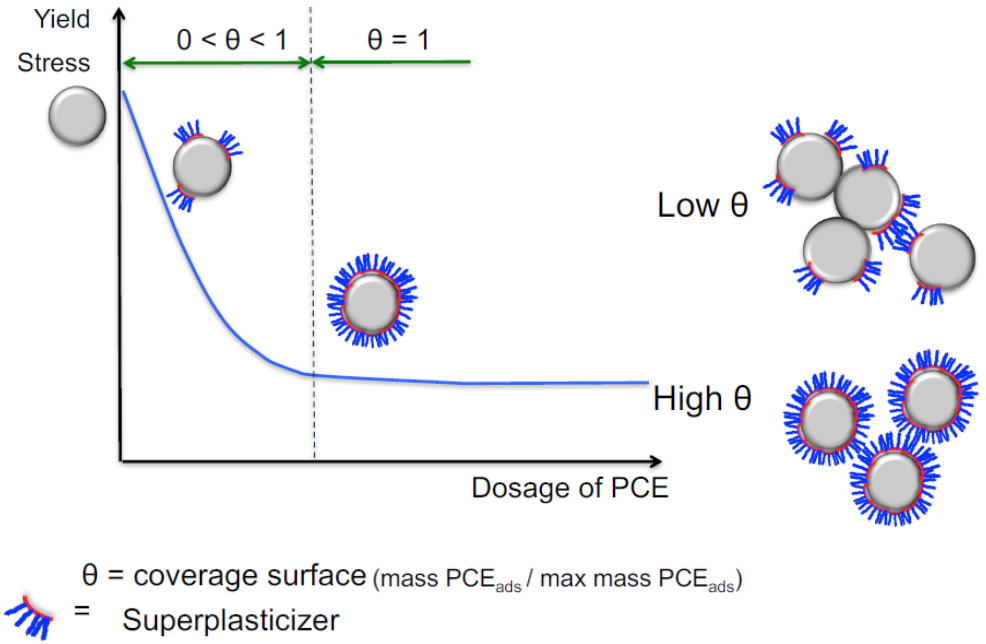
Adsorption

- Adsorption behaviour of PCEs is represented by adsorption isotherms (adsorbed polymer vs. polymer remaining in solution) – Langmuir model
- Adsorbed polymer vs. dosage (up to a certain dosage, a certain and fixed amount of PCE adsorbs)



Houst et al, Cement and Concrete Research, 38, 2008

Adsorption – Surface coverage and yield stress



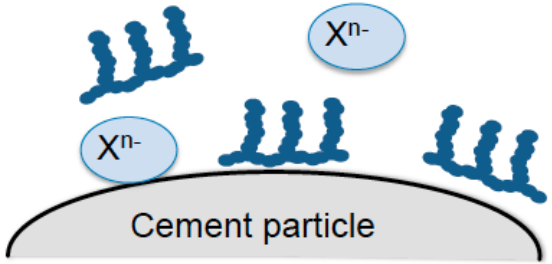
Dr. Mantellato, PhD thesis, ETHZ 2017

Factors affecting PCEs adsorption

- PCE molecular mass and molecular architecture (backbone chemistry and length, side chains length, C/E ratio,..)
- PCEs do not adsorb homogenously on the cement particles
  - **Preferential adsorption onto aluminate phases (highest affinity for ettringite)**
- Precipitation of PCE with the hydrates (organo-aluminate phases)
- Change of specific surface area (SSA)
- Adsorption onto clay minerals
- Competitive adsorption

Competitive adsorption

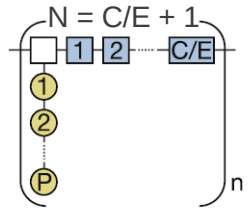
- When more than one species wants to adsorb on the same surface
- In principle any anionic species can compete with each other (sulphates, hydroxides, chlorides, retarders, superplasticizers, viscosity modifying admixtures, ...)



X^{n-} = OH^-, SO_4^{2-}, etc.

Courtesy of Dr. Palacios (IETcc-CSIC)

Competitive adsorption

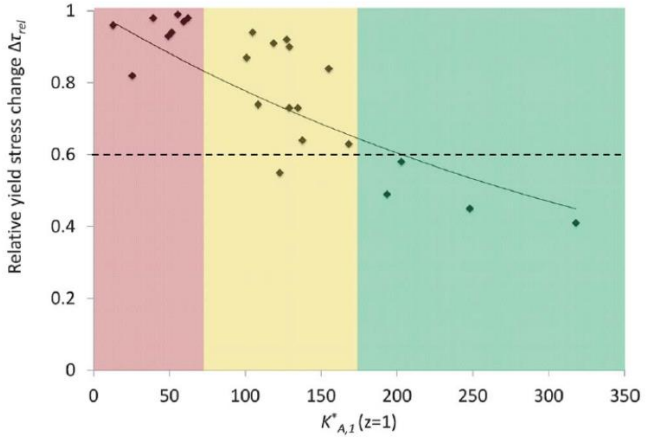


Sensitivity to sulphates

- Increase in sulphate concentration in solution reduces PCE adsorption and fluidity of cement pastes
- Sulphate sensitivity is related to the PCE molecular architecture
- Sulphate Sensitivity Parameter (SSP):

$$P^{4/5}N^{3/5}(N-1)^{-2}$$

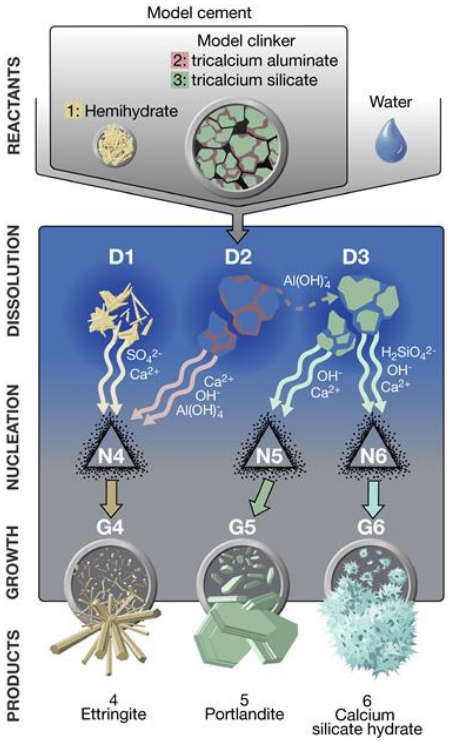
Sensitivity to hydroxides

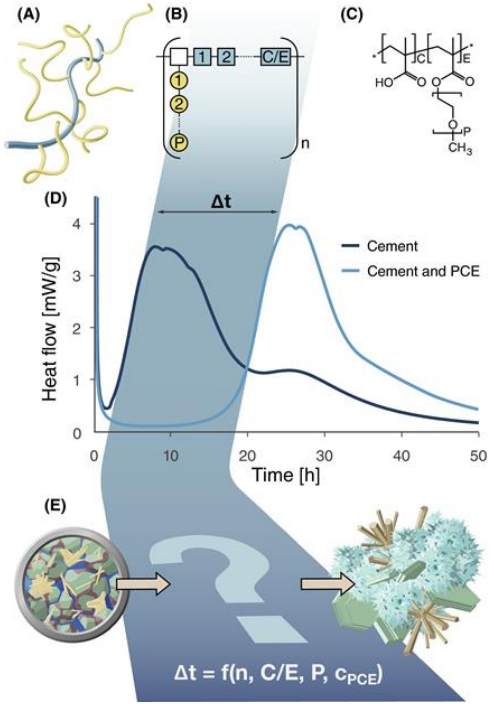


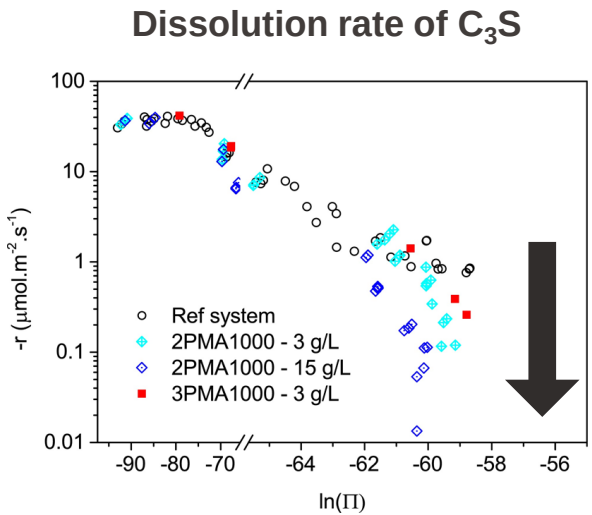
$$\Delta\tau_{rel} = \frac{\tau_{SP,OH^-} - \tau_{SP}}{\tau_{SP,OH^-}} \qquad K_{A,1} \propto \frac{z^2(N-1)^2}{nP^{9/5}N^{3/5}}$$

Yamada et al, Cement and Concrete Research, 31, 2001; Zimmermann et al, 2009; Flatt et al, 2009; Marchon et al, Soft Matter, 9, 2013

Impact of PCE on cement hydration



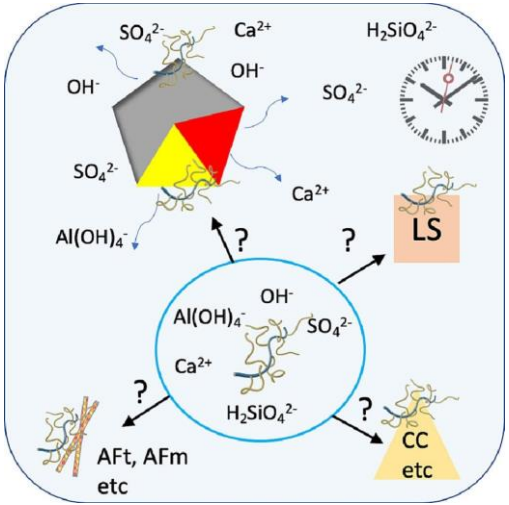




Marchon et al, Journal of the American Ceramic Society, 100, 2017

PCE and blended cements

- Competitive adsorption
- Extent of PCE adsorption for a given dosage is influenced by the PCE structure, pore solution composition and the nature of the surfaces
  - **Blended cements**: Changes in pore solution and nature of the surfaces
- Where does PCE adsorb in blended cements?
  - Admixture distribution will affect rheology and hydration kinetics
- Also, SSA of blended cements may not be the same as for OPC
  - For a given extent of adsorption, modifies surface coverage and therefore the yield stress
- Variety of SCMs ⇨ most probably no general rule
- For LC3: higher initial PCE dosage, the main issue to solve is the flow loss

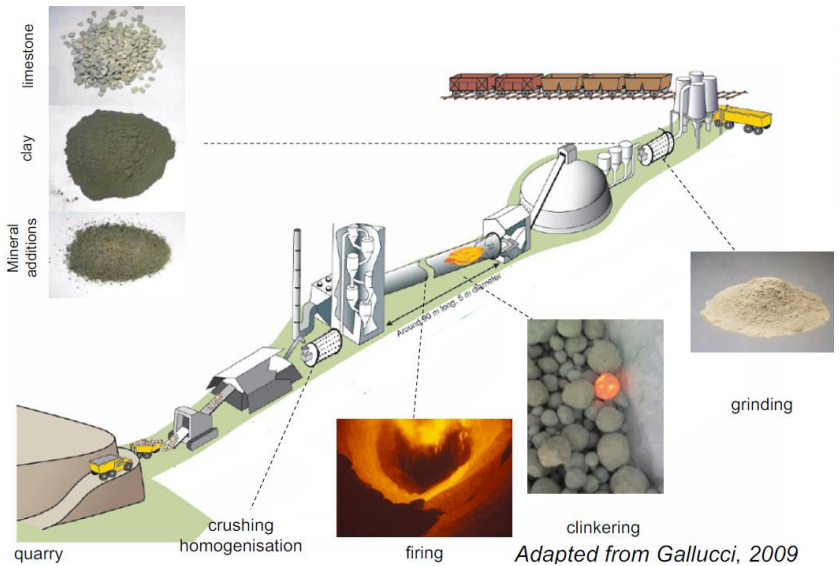


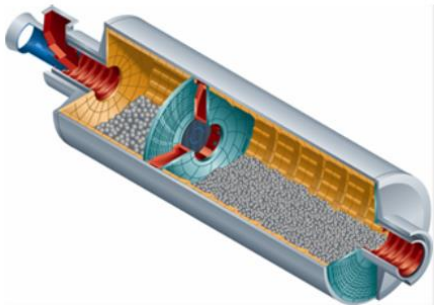
Flatt et al, Cement and Concrete Research, 172, 2023

Commercial admixture formulations

- Classification according to the main action in concrete (EN 206-1, ASTM C494)
- Low-density aqueous solutions, concentration by mass of 15-40%, or powders
- Main factor to consider when selecting a chemical admixture: **final application**
  - **Slump retention** (ready-mix concrete: few to several hours ; precast concrete: first 30 min)
- Single pure SP is NOT often enough to satisfy all the requirements of the final application
  - **Multicomponent products** ⇨ Not trivial (interactions, instability, phase segregation)
- Environmental conditions where the concrete is used
- PCEs tend to produce large air-bubble in concrete (amount and quality is not controlled leading to lower strength) ⇨ **Defoamers or Antifoam agents**
- Stability toward biogenic attack (avoid phase separation, etc.) ⇨ **Biocides**

Grinding aids

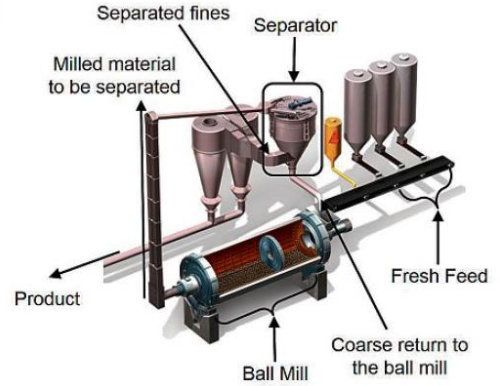


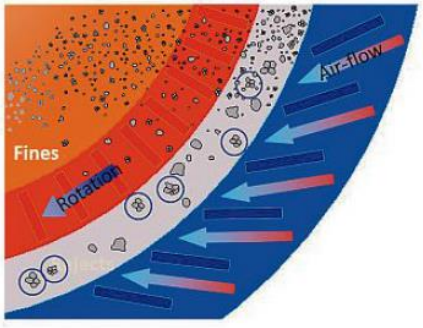


Figures from Dr. T. Mueller and Dr. P. Juilland

Milling and separation process

- Milling station (ball mill) coupled with a cyclone separator that separates the fine fraction from the coarse one
- The coarse part is fed back into the mill, the fine one is the final product
- Milling occurs at 90-120 °C due to mechanical impact. T in the separator is ~90 °C



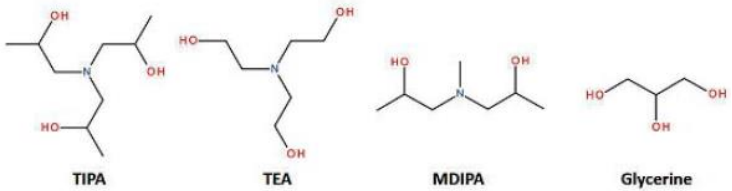


Why do we add grinding aids?

Heller et al, ZKG International, 40, 2011; Mishra et al, Chimia, 71, 2017

Grinding aids

- Main benefits:
  - Reduction of energy consumption during milling
  - Increase in grinding efficiency
  - Minimize the environmental impact
- They modify surface properties of clinker phases
- Their main action is to disperse ground particles
  - Reducing agglomeration
  - Increasing efficiency of the cyclone separator (large particles are fed back to the mill)
- Common grinding aids: triisopropanolamine (TIPA), triethanolamine (TEA), N-methyl-diisopropanolamine (MDIPA), Glycerine
- Extremely low dosage



Grinding aids

Adsorption of grinding aids occurs on the hydroxylated clinker surface, mainly due to complexation of superficial calcium ions, hydrogen bonds and multipolar interactions

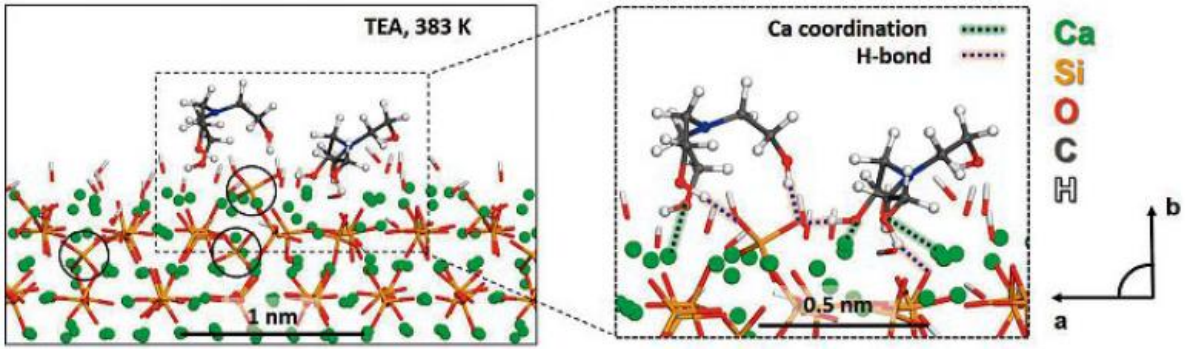


Fig. 10. Two TEA (triethanolamine) molecules on the hydroxylated tricalcium silicate surface, showing adsorption by hydrogen bonds and coordination of superficial Ca ions by hydroxyl groups (see inset). Circular highlights indicate surface reconstruction.[7b]

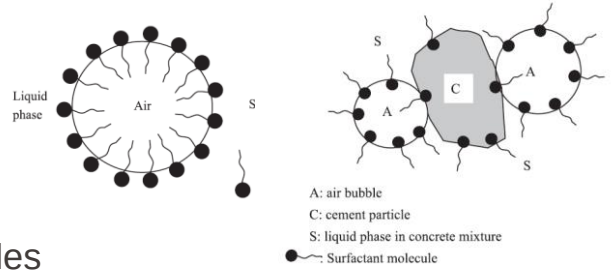
Mishra et al, The Journal of Physical Chemistry C, 117, 20, 2013

Air-entraining admixtures (AEAs)

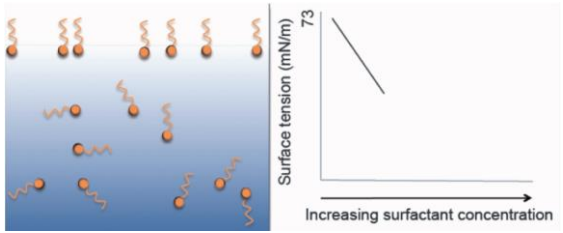
- Protection against **freezing and thawing cycles**
- Air bubbles in concrete are formed during mixing
- Total volume of entrapped air in concrete:
  - < 3% in absence of AEAs (diameter of 0.5–5 mm)
  - 4-8% in presence of AEAs, according to the specifications
- AEAs favor the **formation of numerous stable and finer air bubbles** (diameter of 1–100 µm)
- **Control of the volume of entrained air and the structure of the bubble network** by the selection and the dosage of AEA
- Increase in the volume of air often leads to an increase in workability and a decrease in compressive strength

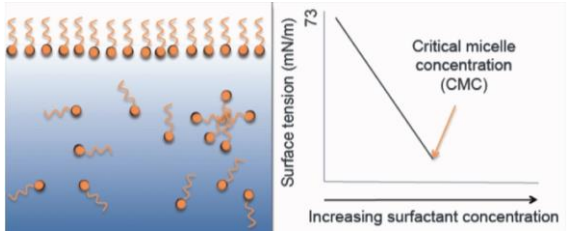
Air-entraining admixtures (AEAs)

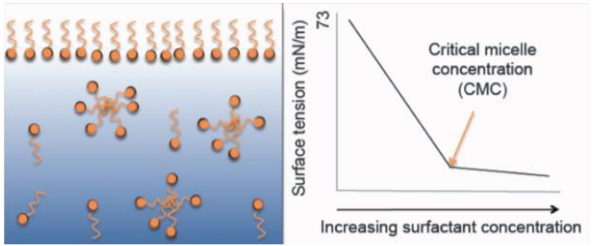
- They are organic molecules of various chemical composition, acting as surfactants
- Hydrophilic termination bound to a hydrophobic chain
- Adsorption at the liquid – vapor interface
  - **Reduction of the air – water superficial tension**
- Adsorption on solids partially supports the stabilization of air bubbles



Du & Folliard, 2004







Tunstall et al., Cement and Concrete Research, 92, 2017

Air-entraining admixtures (AEAs)

- The spacing of the air bubbles affects the protection against freeze and thaw (**spacing factor**)
  - > 700 µm in non-air-entrained conventional concrete
  - 100–200 µm in concrete with satisfactory network
- The air entrainment is less efficient at high water dosages
- Higher **cement fineness**, higher dosage of AEA to obtain a certain volume of air
- Blast furnace slag and fly ash usually decrease the AEA efficiency
- Possible physicochemical **interactions with other admixtures** (SPs, retarders, accelerators, etc.)
  - Difficult to give general recommendations due to the variety and complexity of molecules

Shrinkage

1. Plastic shrinkage
2. Autogenous and chemical shrinkage
3. Drying shrinkage

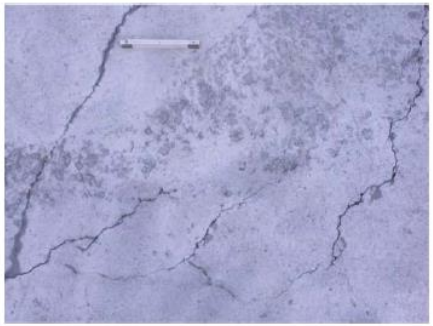
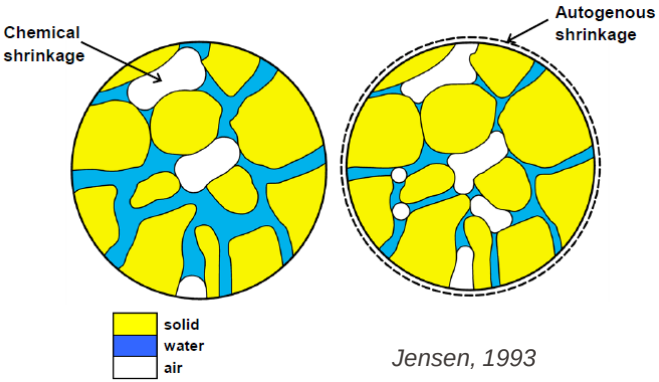


Photo from Dr. A. Leemann (EMPA)

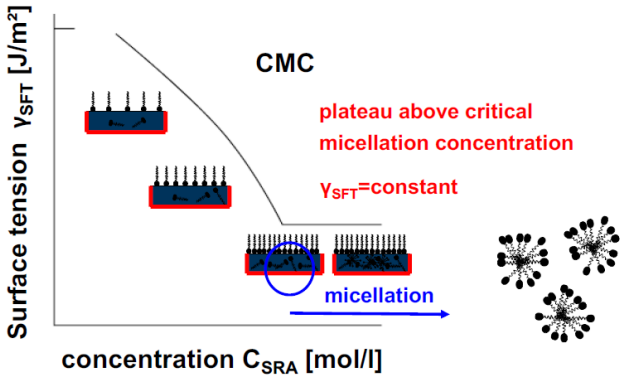


Jensen, 1993

Photos from Dr. R. Loser (EMPA)

Shrinkage-reducing admixtures (SRAs)

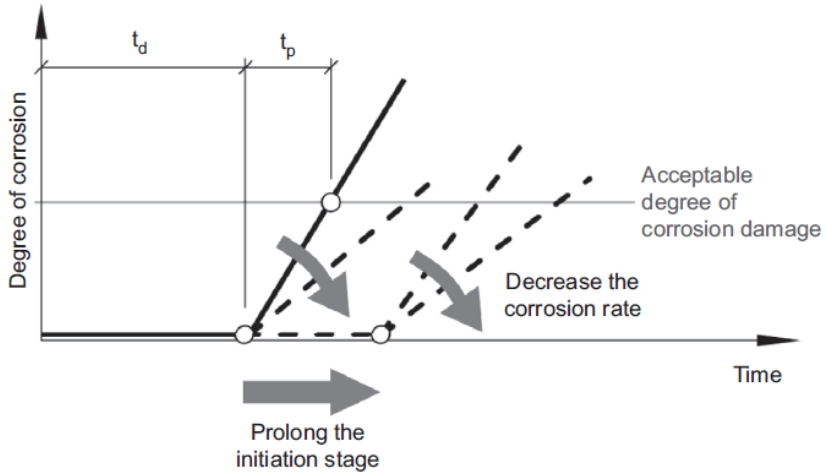
- SRAs are surfactants
- They decrease the surface tension of the pore solution or water film covering the solid surfaces exposed to drying
- Dosage can be between 1–2% by weight of binder
- Similarities between AEAs and SRAs (both contains amphiphilic compounds) BUT different mode of action!
  - AEA: partial stabilization of air bubbles due to adsorption of AEAs onto solids
  - SRA: efficient only by adsorption at the liquid-vapour interface



Dr. A. Eberhardt, PhD thesis, 2011

Corrosion inhibitors

- Added to prolong the service life of reinforced concrete
- They are added with the mixing water and they **act primarily at the steel surface** (chemical or electrochemical interaction with the steel)
- In principle they **delay the corrosion onset** (by a factor of 2–3 in time) and **reduce the corrosion rate** (most research on the first, due to design codes)



Elsener & Angst, 2016

Corrosion inhibitors

Type of inhibitors

- Anodic inhibitor:
  - Affect the anodic reaction
- Cathodic inhibitor:
  - Affect the cathodic reaction
- Mixed inhibitor:
  - Affect both reactions

Mechanism of action of inhibitors for chloride-induced pitting corrosion

- By enhancing passivity
- By the formation of a film prior to the chloride ingress
- By buffering the pH in the local pit environment
- By competitive adsorption on the surface between inhibitor and chloride ions
- By competitive migration of inhibitor and chloride ions into the pit

Corrosion inhibitors

Factors to consider

- **Concentration-dependent effect**:
  - Critical ratio inhibitor – chloride has to be exceeded
- Difficult to check whether the inhibitor is really present at the reinforcement
- Consider the long-term efficiency
  - Leaching
  - Evaporation of volatile components
  - Consumption of the inhibitor
- Some inhibitors show **secondary effects** on the properties of concrete (fresh and hardened)
- Major difficulty in an independent evaluation of a commercial inhibitor:
  - **Unknown or uncertain composition**

General remarks

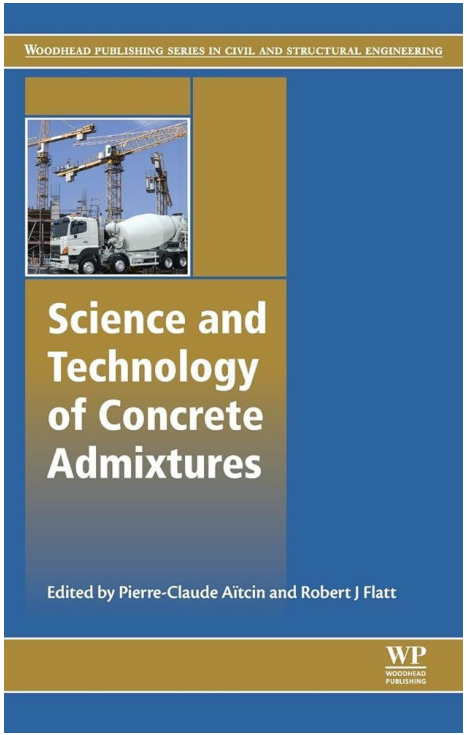
- Chemical admixtures may have secondary effects on the properties of concrete
- Interactions between different chemical admixtures
- Compatibility issues
- Commercial products are often blends of several compounds tailored for specific applications
- Effect of supplementary cementitious materials (SCMs)
- Many open questions are yet to be answered...

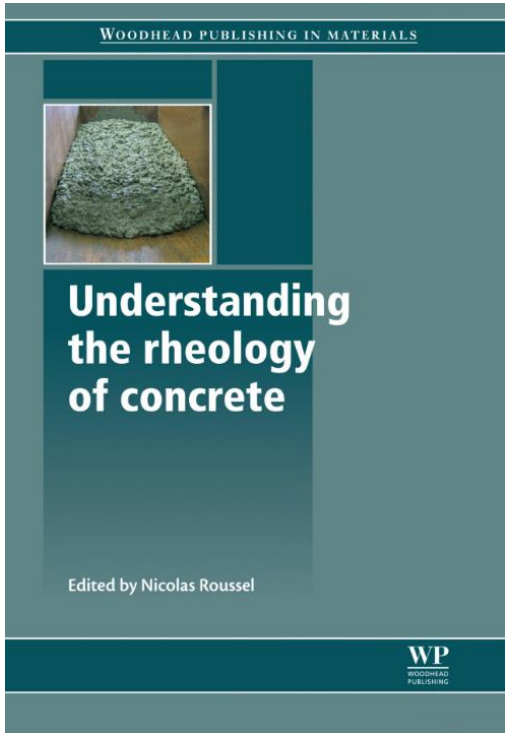
Learning objectives

Now, at the end of this class, you are able to...

- **Identify** the main chemical admixtures in concrete technology
- **Describe** their effect on cement and concrete properties, their mechanism of action and their interactions with other chemical admixtures
- **Suggest** what admixture(s) shall be used in a specific application, taking into account environmental conditions
- **Relate** the use of chemical admixtures to environmentally friendly concrete and sustainability

Recommended literature





Course schedule

Week #	Class date	Title	Lecturer
1	11/09/2024	Introduction and Literature Review	Prof. Karen Scrivener / Dr. Alastair Marsh
2	18/09/2024	Durability	Dr. Beatrice Malchiodi
3	25/09/2024	Cement hydration	Prof. Karen Scrivener
4	02/10/2024	Characterisation	Dr. Federica Boscaro
5	**09/10/2024**	**Presentation 1**	
6	16/10/2024	Admixtures	Dr. Federica Boscaro
7	**30/10/2024**	**Presentation 2**	
8	06/11/2024	Life cycle analysis for cementitious materials	Dr. Alastair Marsh
9	13/11/2024	Limestone calcined clay cements (LC^3)	Dr. Franco Zunino
10	20/11/2024	Concrete design	Dr. Beatrice Malchiodi
11	27/11/2024	Sustainability appraoches for construction	Dr. Alastair Marsh
12	04/12/2024	Concrete structures / Q&A on Presentation 3	Prof. David Ruggiero
13	**11/12/2024**	**Presentation 3**	
14	18/12/2024	Re-use & standardization	Prof. David Fernandez / Prof. Corentin Fivet

Questions?

Advanced cementitious materials, MSE-420

Lecture 6: Chemical admixtures use in concrete

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16th October 2024