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Fundamentals in Building Industries

Cement Chemistry, Chemistry of Admixtures

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Important mineral binders – Nowadays and in former times

Gypsum ($CaSO_4 \cdot 2\,H_2O$)
- Known since 9000 b.C.
- 1st traces of application: Catal Huyuk

Lime stone ($CaCO_3$)
- Since 5600 – 5000 b.C.
- 1st traces of application: Region of the river Danube

Portland cement (PC, PZ, CEM)
- Since 1824/1843 invention of J. Aspdin, improved by W. Aspdin
- Portland = natural stone from the island Portland

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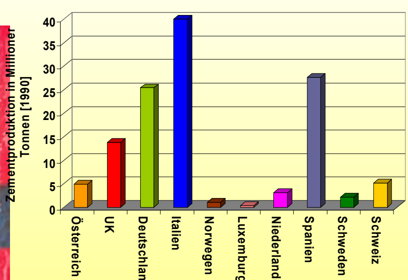
The Portland cement – important for Economy and Society



Production of Portland cement – Raw materials

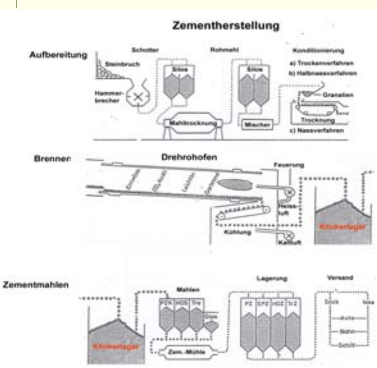
Raw materials for cement production:

- **limestone ($CaCO_3$)**
- **clay containing marl (SiO_2, Al_2O_3, Fe_2O_3)**
- **lime containing marl ($CaCO_3$,SiO_2)**

➔Ideal chemical raw material composition is calculated by various parameters (e.g. KSt)

KSt = Kalkstandard ~ lime standard

Production process:



Primary combustible:

- Mineral coal powder
- Brown coal powder
- Fuel oil
- Natural gas

Secondary combustible :

- Waste materials (e.g. used tires)

Energy demand: 3000-6000 KJ/kg

Chemical reactions of the production of Portland cement clinker

Deacidification: $CaCO_3$ ➔ $CaO + CO_{2(g)}$

Thermal synthesis of the clinker components:

$3\ CaO + SiO_2$ ➔ Ca_3SiO_5

$2\ CaO + SiO_2$ ➔ Ca_2SiO_4

$3\ CaO + Al_2O_3$ ➔ $Ca_3Al_2O_6$

$4\ CaO + Al_2O_3 + Fe_2O_3$ ➔ $Ca_4Al_2Fe_2O_{10}$

Stoichiometrie ➔“elements“ and „masses“

Portland cement clinker

Name	formula 1	formula 2	formula 3
Tricalciumsilicate	Ca_3SiO_5	$3\ CaO \cdot SiO_2$	**C_3S**
Dicalciumsilicate	Ca_2SiO_4	$2\ CaO \cdot SiO_2$	**C_2S**
Tricalciumaluminate	$Ca_3Al_2O_6$	$3\ CaO \cdot Al_2O_3$	**C_3A**
Tetracalcium-aluminatferrite	$Ca_4Al_2Fe_2O_{10}$	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	**C_4AF**

C = CaO	S = SiO_2	A = Al_2O_3
F = Fe_2O_3	$\overline{C}$ = CO_3	$\overline{S}$ = SO_3

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Composition of the Portland cement clinkers

Bezeichnung des reinen Minerals	Formel	Abkürzung	Bezeichnung des im Klinker vorliegenden Minerals
Tricalciumsilicat	$3\ CaO \cdot SiO_2$	C_3S	Alit
Dicalciumsilicat	$2\ CaO \cdot SiO_2$	C_2S	Belit
Tricalciumaluminat	$3\ CaO \cdot Al_2O_3$	C_3A	Aluminat
Calciumaluminatferrit	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$C_2(A,F)$	Aluminatferrit

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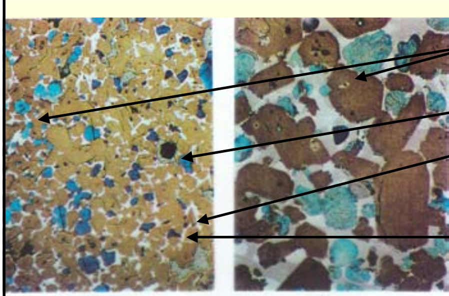
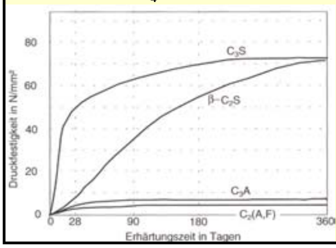
Portland cement clinker – Polished microsection



Portland cement clinker – cement technological properties

C_3S: Early and late stiffness
C_2S: late stiffness and low heat of hydration
C_3A: Early stiffness and high heat of hydration
C_4AF: corrosion resistance / sulfate resistance



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Portland cement clinker - composition

Labelling	Min.-Value	Max.-Value	Average
C_3S	60	70	65
C_2S	4	25	16
C_3A	1	13	11
C_4AF	1	16	8

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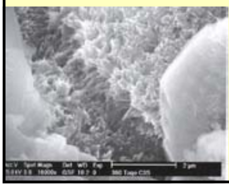
Portland cement – Clinker hydration

The different clinker components react differently
- **C_3S/C_2S: Formation of CSH-Gel**
- **C_3A: Formation of calciumaluminates**
- **C4AF: Formation of calciumaluminatferrithydrates**

Portland cement – hydration of C_3S/C_2S

Equitation: $C_3S + (y+z)\,H \rightarrow C_xSH_y + z\,CH$
Example: $2\,C_3S + 6\,H \rightarrow C_3S_2H_3 + 3\,CH$



- The CSH-gel has no explicit stoichiometry
- Changes shape and composition during hydration
- high specific surface (200g/m^2)

Portland cement – Hydration of C_3A

Addition of water: $2C_3A + 21\,H \rightarrow C_4AH_{13} + C_2AH_8$
Transformation: $C_4AH_{13} + C_2AH_8 \rightarrow 2\,C_3AH_3 + 3\,CH$

In absence of sulfate C3A hydrates in thin plates (calciumaluminate hydrates)
→ Result: quick stiffening of the material

Portland cement – Hydration of C_3A in presence of $CaSO_4$

Formation of ettringite

Addition of water: $C_3A + 3\,C\overline{S}H_2 + 26\,H \rightarrow C_3A \cdot 3\,C\overline{S} \cdot 32\,H$
ettringite

- In presence of gypsum the water-rich compound ettringite is formed
→ **needle-structure**
Result: Decrease of the reactivity of the C_3A-Phase

Portland cement – Hydration of C_4AF in presence of $CaSO_4$

Water addition: $C_4AF + 12\ C\overline{S}H_2 + 110\ H \rightarrow 4\ [C_3(AF) \cdot 3\ \overline{CS} \cdot H_{32}] + 2\ [(A,F)H_3]$
= AFt-Phase

Transformation: $3C_4AF + [C_3(AF) \cdot 3\ \overline{CS} \cdot H_{32}] + 14\ CSH_2 \rightarrow 6\ [C_3(AF) \cdot \overline{CS} \cdot H_{32}] + 2[(A,F)H_3]$
= AFm-Phase

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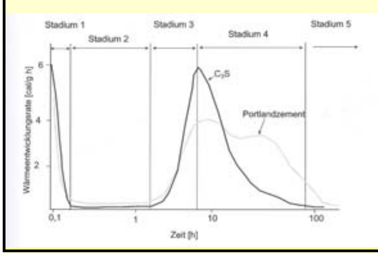
Time scale of hydration



1. Solution- or initial hydrolysis
2. Dormant period
3. Acceleration period
4. Deceleration period
5. Steady period

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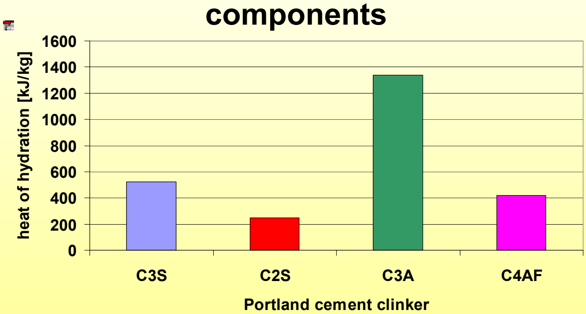
Reaction enthalpy of the clinker components



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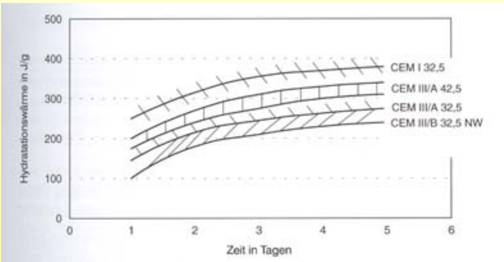
Portland cement – Heat of hydration

Heat of hydration progression depends on type of cement



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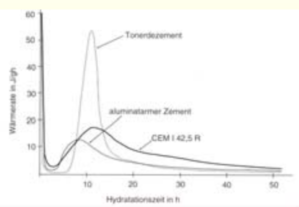
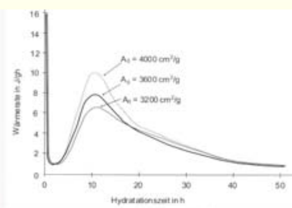
Portland cement – heat of hydration





Type of cement

Cement strength

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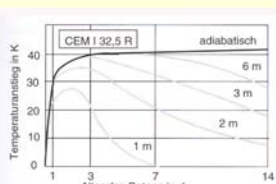
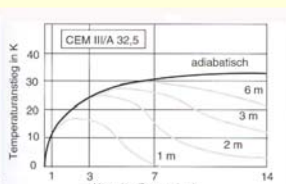
Portland cement – Heat of hydration

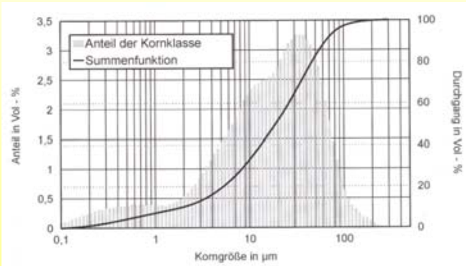
Temperature distribution in a concrete member





Portland cement – Grinding fineness

Particle size distribution measured with laser granulometer



Portland cement – Grinding fineness

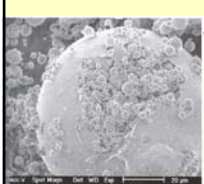
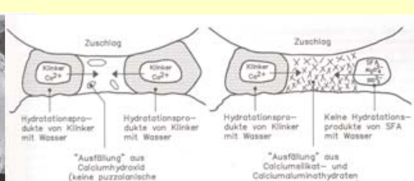
Grinding fineness according to Blaine

Zementart	$R_{90\mu m}$ in %	A_0 in cm^2/g
CEM I 32,5	< 10	2400...4000
CEM I 42,5	< 6	2800...4500
CEM I 52,5	< 1	4000...6000
CEM II /A-P	< 4	3000...5500
CEM III 32,5	< 6	3000...4000
CEM III 42,5	< 3	3300...4500

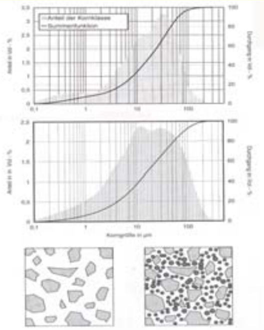
The puzzolanic reaction

0-28 day: $C_3S + H_2O \rightarrow$ CSH-Gel + 3 $Ca(OH)_2$

3-90 day: $Ca(OH)_2 + SiO_2$ (vitreous) + $H_2O \rightarrow$ CSH-gel

Particle size distribution of fly ash

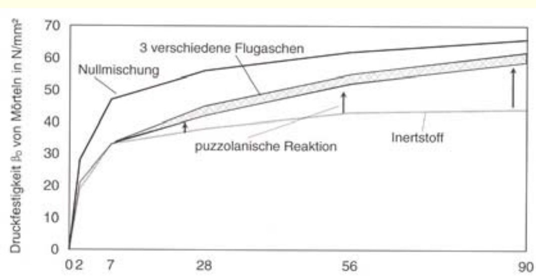


Portland cement CEM I 32.5 R

Fly ash

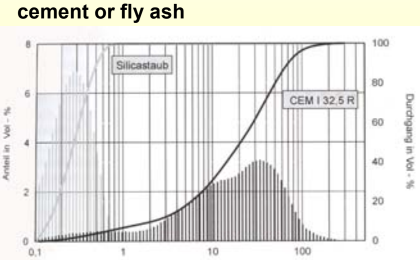
Particle distribution

Fly ash – Strength progression of different mortar mixtures



Silica fume for high performance concrete

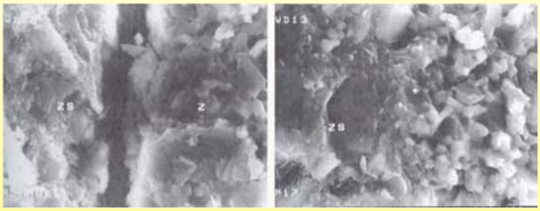
Average particle size distribution is less than Portland cement or fly ash



Silicafume – properties in concrete

Boundary layer aggregate (Z) / cement rock (ZS)

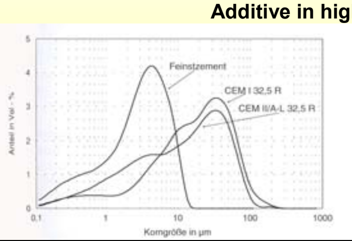
Without silica fume (SF) Silica fume (SF) is added



Special cement: Micro milled cements

Indicator: Grinding fineness and particle size distribution

Applications: Geotechnique (soil strengthening)
concrete repair (crack compression)
Additive in high performance concrete

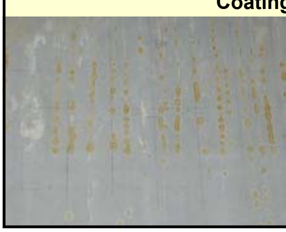


Disadvantage: Price is 5-10 times higher compared to Portland cement

Special cement: White cement

Indicator: colour (iron content < 0.5%)

Application: coloured mortars
„Art at construction site“ (sculptures)
Coating materials



Disadvantage: price is higher compared to Portland cement

Concrete admixtures

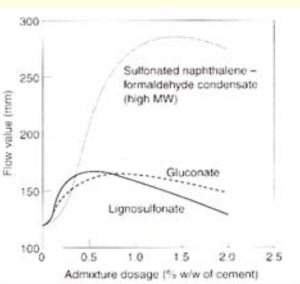
-Plasticizer

-Air entraining agents

-Retarder/Accelerators

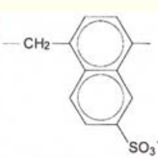
-Sealer (increase concrete density)

Plasticizer



Concrete plasticizer were added either...
... to increase workability by same W/C-ratio...
... or ...
... to reduce W/C-ratio by same workability.

Types of high performance plasticizers



Napthalin-Formaldehyd-Kondensate

Melamin-Formaldehyd-Kondensate

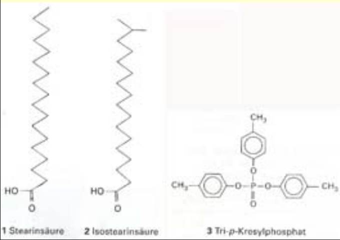
High performance plasticizers are boundary layer active substances, bearing a hydrophilic and a hydrophobic part.

Applicated high performance plasticizers:

- Sulfonated melamine-formaldehyde-resins
- Sulfonated napthaline-formaldehyde-resins
- modified ligninsulfonates
- Sulfonated polymers (polystyroles, copolymers)
- ...

Boundary layer active substances

Boundary layer active substances develop their properties between two different phases.

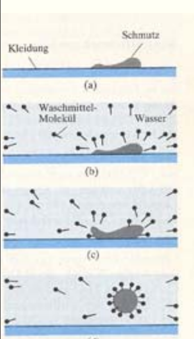


Tensides are made up of a polar (hydrophilic) and a non-polar (hydrophobic) part. Added to water they reduce the surface tension

Manufacture of boundary layer active substances

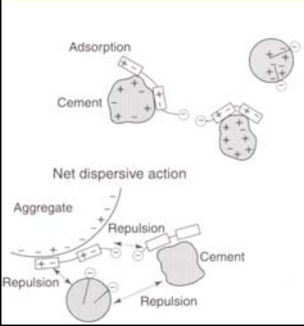
„Soaps“ were crafted of fat and alkaline solutions. Thereby soft soap comes out. By treating with sodium chloride or potassium chloride curd soap is formed.

Properties of wash-active substances



The hydrophobic endings of the soap molecule were adsorbed at the dirt particles and lift it off. The dirt particle is suspended and can be carried away. In contact with hard water insoluble lime soap is formed.

Plasticizers: Mode of action



The properties of high performance plasticizers are based on:

- reducing the surface tension of water
- Dispersion of the cement particles through absorption of the plasticizer molecules on the particle surface

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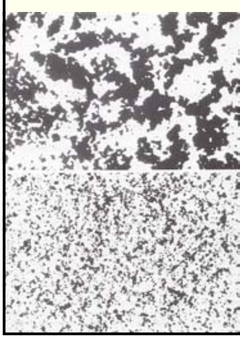
Plasticizers: Mode of action



Cement particles without plasticizer

Cement particles with plasticizer

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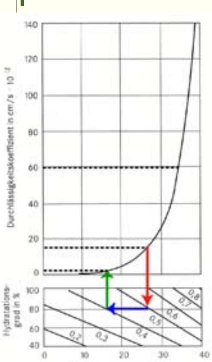

Permeability of cement based materials – properties of plasticizers

The application of plasticizers can reduce the W/C-ratio by same workability.

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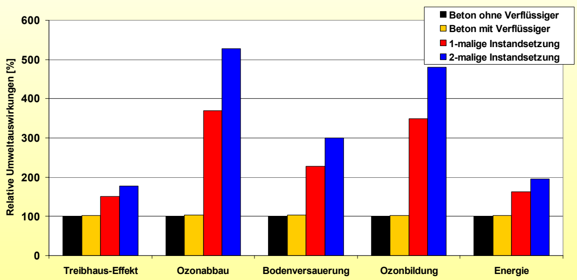
Environmental aspects from the application of plasticizers



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Freeze damage to cement based materials

Through freeze properties, particularly in the presence of thaw salts, can damage cement based materials mechanically within short periods.

Example:
Top of a bridge

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Effect of freeze-thaw-circles on cement based materials

- Ice formation is associated with 9% increase of volume
- Crystallisation pressure > tensile strength of material
- Ice-based expansion of the material leads to breaking-up and finally to mechanical destruction

Result:
Breaking-up and structural damage

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Freeze-thaw-circle-based damages

1. Properties of soluted salts

- Soluted salts increase the vapour pressure and lower freezing point
- Results: lower vapour pressure decline between little and bigger pores
- Lower temperature needed for ice formation in larger pores necessary
  ➔ decrease in water redistribution

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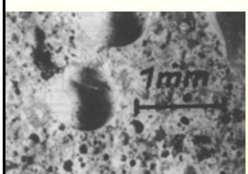
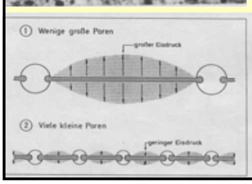
Air entraining agents



The freeze and freeze thaw salt resistance of cement based materials can be increased by the use of air entraining agents.



Applicated systems:

- **Air entraining agents**
- **Micro hollow balls**

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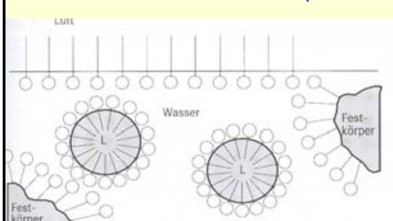
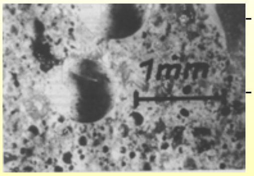
Types of air entraining agents

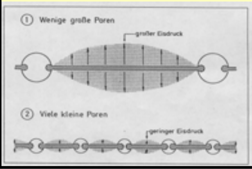
- **Substances based on vinsol resins (alcohol soluble)**
- **Fatty acids**
- **Alcylsulfates**
- **Fatt-alcohol-polyglykolethersulfates**
- **Micro hollow balls – MHK (air filled polymer balls)**



Properties of air entraining agents



- Expand volume accessible for water (water vapour transport because of different partial pressure)
- Capillare reducing effect



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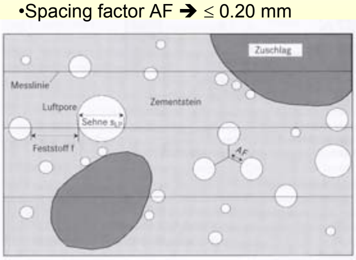
Requirements for air entraining agents

Characterisation of the air pore system

•Total air pore content L ➔ between 3.5 and 4% in fresh concrete
•L300-content ➔ air pores between 10 und 300 µm, ≥ 1.5 Vol-%
•Spacing factor AF ➔ ≤ 0.20 mm



Air entraining agents reduce tensile strength but increase workability
➔ **partial compensation**

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Retarder

Retarder were added by ...

- **... high temperature**
- **... manufacture of large concrete members**
- **... Ready-mix concrete**

... to gain adequate workability

Types of retader

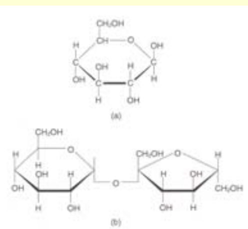
1. **Substances which form hardly soluble Ca-salts or Ca-complexes**
2. **Macromolecules which form colloids**

1. Group
- Sodium- and potassiumphosphates
- Sodiumgluconate
- Saccharose
- Zincoxide

2. Group
- Methylcellulose
- Dextrine
- Caseine

Retarder: Mode of action

- Retarder form complex calcium compounds and inhibit the over-saturation with calcium hydroxide. E.g.: glucose
  $3 \cdot 10^{-4}$ cm^3 glucose-solution for 1 cm^3 PC
- The over-saturation can also be prevented by the formation of hardly soluble compounds (ZnO).
- Other compounds form hardly soluble salts on the surface and therefore prevent the access of water (salicyl acid)



Accelerators

Accelerators were added...

- **... to strip the forms earlier**
- **... To strip the forms by varying temperature at the same time**
- **... to protect the concrete from freeze in winter times**
- **... to shorten the setting time by special applications (invasion of water)**
- **... To gain quick setting shotcrete**

Types of accelerators

Accelerators cause a faster solution process of the clinker components and therefore a faster hydration

1.Group

Compounds increasing the hydroxide concentration
NaOH, KOH, Na_2CO_3

2. Group

Compounds which form calcium silicate hydrates

alkali silicates

3. Group

Compounds increasing the Ca^{2+} concentration

$CaCl_2$, calciumformiat

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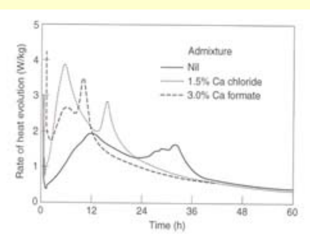
Accelerators: Mode of action

The mode of action of accelerators is not fully revealed. Presumably they effect the solution of the clinker components and therefore the speed of hydration.



- The C_3S-phase can be activated by chloride, nitrate, nitrite, formiate, etc. supplemented by the effect of the cations
- $CaCl_2$ is a very effective activator for C_3S but forbidden in reinforced concrete