Solid construction materials

Cement

Portland cement (silicate cement)

Aluminous cement (bauxite cement)

Magnesia cement (Sorel cement)

Portland cement: produced from **limestone** ($CaCO_3$) and **clay** (SiO_2, Al_2O_3, Fe_2O_3), **gypsum** ($CaSO_4 \cdot 2H_2O$)

- Main component: calcium silicates → calcium-silicate-hydrate (CSH)

Aluminous cement: produced from **limestone** ($CaCO_3$) and **aluminous minerals**

- Main component: calcium aluminates → calcium-aluminate-hydrate (CAH), instable, generally recrystallizes
- Used as base for fire-resisting concrete products

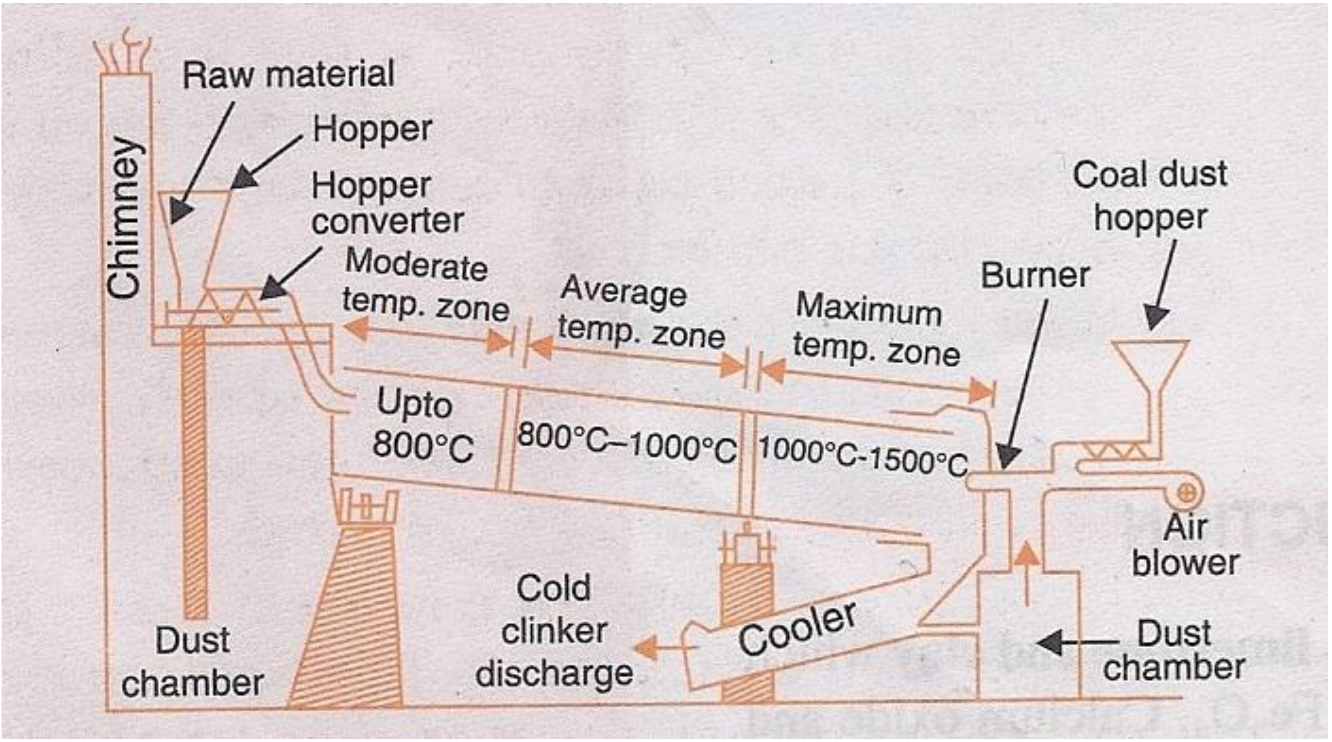
Magnesia cement: softly fired, non-shrinked MgO (made out of $MgCO_3$ at high temperature with addition of $MgSO_4$)

- Used for making heated and plastic coated floors

Portland cement

Grinding and milling of minerals, then firing it in a rotary kiln

CLINKER



Portland cement

- 70-110 °C ⇒ free water evaporates
- 400-600 °C =>clay decompostion → SiO_2, Al_2O_3
  dolomite ($CaMg(CO_3)_2$ decomp. in MgO, CaO, CO_2
- 650-900 °C => $CaCO_3$ reacts with SiO_2 →**belite (Ca_2SiO_4**)
- 900-1050 °C ⇒ rests of $CaCO_3$ decompose → CaO, CO_2
- 1300-1450 °C => partially (20-30%) melting, belite reacts with the rest of the CaO → **alite (Ca_3SiO_5)** will be produced

Because of the melting the material agglomerates and becomes lumpy. The diameter of the material will be of 1-10mm. These agglomerates are called CLINKER. It is cooled and stored in a dry place

Portland clinker + gypsum, milling → Portland cement

Portland cement components

Typical constituents of Portland clinker plus gypsum		
Clinker	CCN	Mass %
Tricalcium silicate $(CaO)_3 \cdot SiO_2$	C_3S	45–75%
Dicalcium silicate $(CaO)_2 \cdot SiO_2$	C_2S	7–32%
Tricalcium aluminate $(CaO)_3 \cdot Al_2O_3$	C_3A	0–13%
Tetracalcium aluminoferrite $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	0–18%
Gypsum $CaSO_4 \cdot 2\ H_2O$	$C\bar{S}H_2$	2–10%

Portland cement components

Typical constituents of Portland cement		
Cement	CCN	Mass %
Calcium oxide, CaO	C	61–67%
Silicon dioxide, SiO_2	S	19–23%
Aluminum oxide, Al_2O_3	A	2.5–6%
Ferric oxide, Fe_2O_3	F	0–6%
Sulfur (VI) oxide, SO_3	$\overline{S}$	1.5–4.5%

Composition of clinker minerals

Silicates

- **Alite (C_3S)** **tricalcium-silicates**: $3CaO \cdot SiO_2$
  - hexagonal crystals with Al and Mg impurities
  - 37-60%
  - **great initial strength**
- **Belite (C_2S)** **dicalcium-silicates**: $2CaO \cdot SiO_2$
  - spherical crystals + other ions in small quantity
  - 15-37%
  - small initial, then **good after-strength**, good initial tensile strength
  - resistant to sulphate

Sulphates

- **Gypsum (dihydrate)** $CaSO_4 \cdot 2H_2O$ **(CŜ)**
- **Plaster (hemihydrate)** $CaSO_4 \cdot 0.5H_2O$
- **Anhydrite** $CaSO_4$

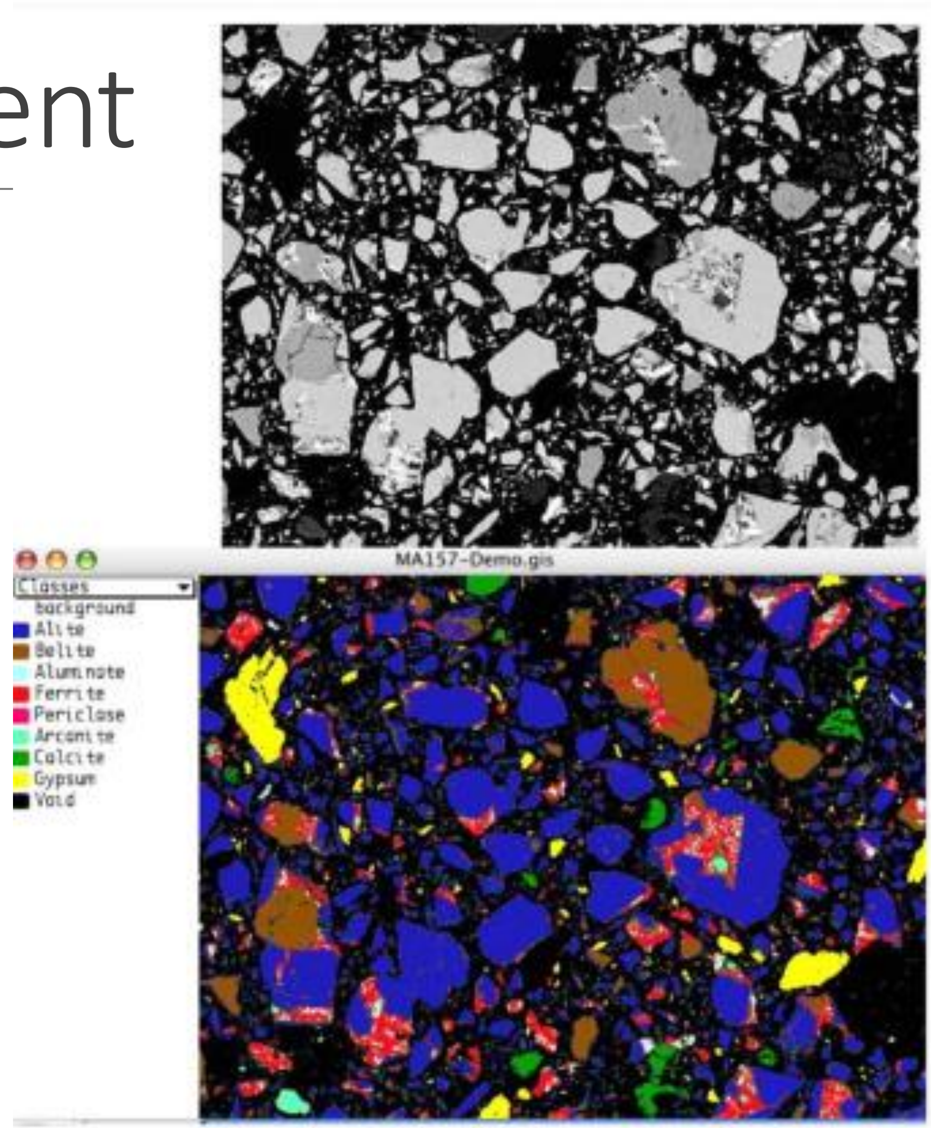
Aluminates

- **Tricalcium-aluminate** **C_3A** - $3CaO \cdot Al_2O_3$
  - 7-15%
  - **fast solidifying**, heat generating, that has to be attenuated by addition of gypsum.
  - **cements with small tricalcium aluminate are resistant to sulphates**
- **Tetracalcium-aluminate-ferrite** **- celit C_4AF** -$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
  - small strength
  - slow solidifying

Portland cement

Texture of the clinker

- Alite
- Belite
- Aluminate
- Ferrite
- Periclase
- Arzenit
- Calcite
- Gypsum
- Void



Portland cement

Curing of cement/concrete

- 1. phase: settling
- 2. phase: solidifying
- 3. phase: aging (beyond 28)

HYDRATION (C-S-H) – 1., 2.

Saturated colloid solution→ Supersaturated colloid solution → gel layer at the surface of the grains→ crystallization (beyond 28)→ **cement stone** (stable above pH 7) – 2., 3.

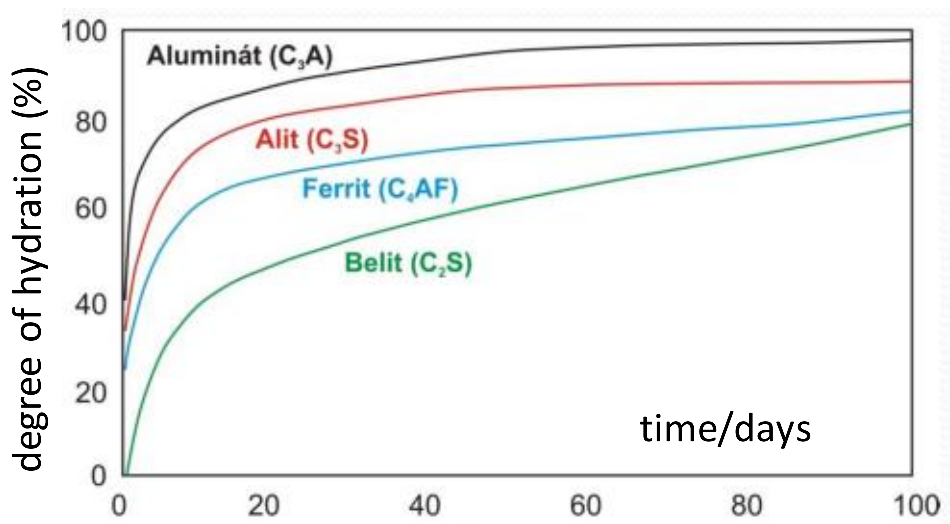
$Ca(OH)_2$ is formed – 3. phase

Hydration

C_3S
C_2S
C_3A
$C\hat{S}$

+ H_2O → fluid phase → supersaturated solution

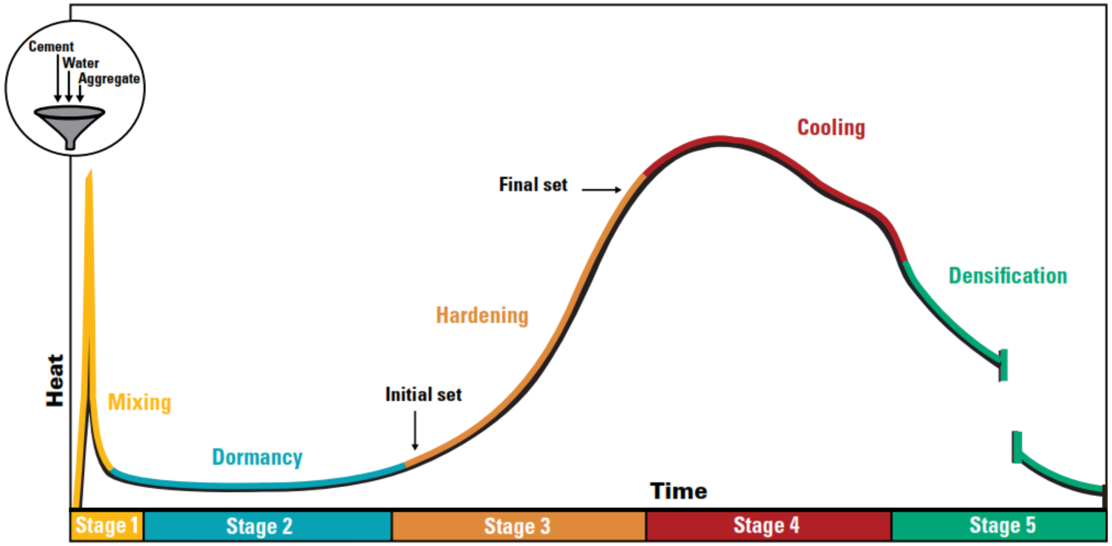
→ solid phase CSH



Hydration

Phases:

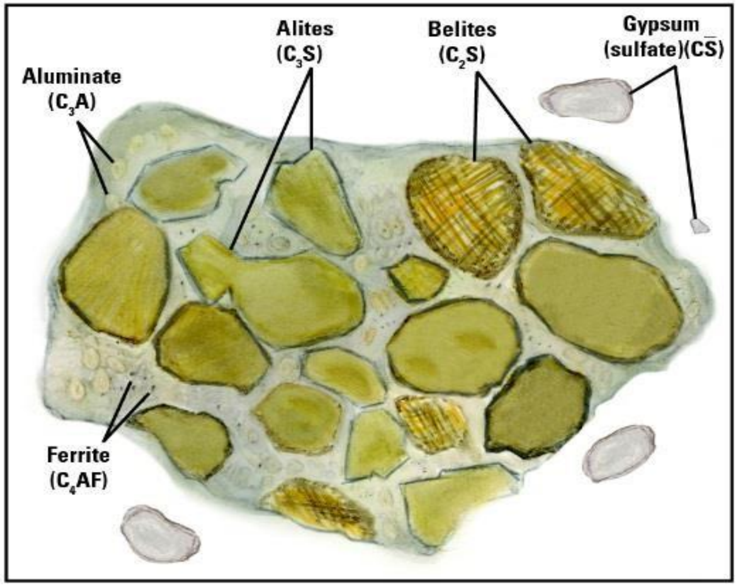
- 1. Mixing
- 2. Induction (dormancy)
- 3. Hardening
- 4. Cooling
- 5. Densification



hydration can take place only with **water**, the cement mixture with other solutions than water do not solidify

the hydration starts at the outer layer of the cement grains, the layer that takes place in the hydration is of **10-15 microns**

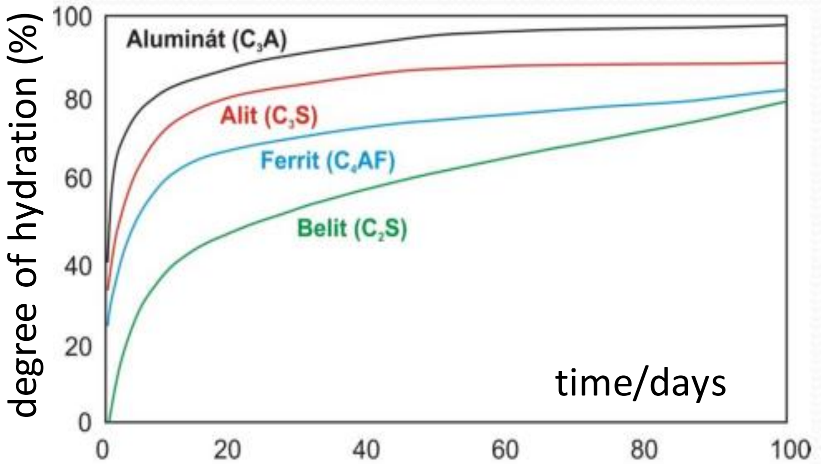
the grain size and the water/cement ratio influences the hydration. **Smaller grain size** more complete hydration, **water/cement ratio** < 0.32, not enough water for the process



1. Mixing

C_3A and gypsum ($C\hat{S}$) react very rapidly with water, **aluminates** and **gypsum** start to form hydrated products (**aluminate hydrates**), and ettringite starts to form, forming a gel layer around the grains

the **coating slows** the aluminate reaction by limiting water's acces to the grains, the heat release drops



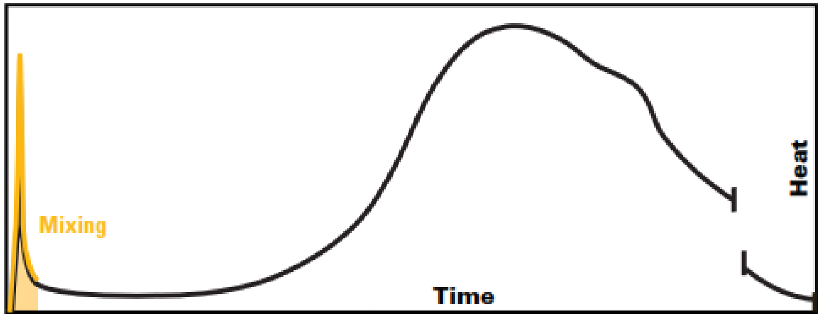
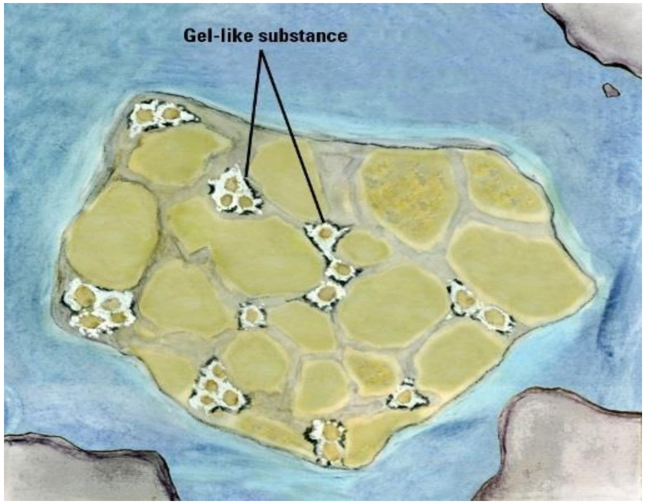


Figure 4-3. A very brief heat spike occurs during mixing.



1. Mixing

$C_3A + 3\ CaSO_4 \rightarrow$ **ettringite**

Gypsum is added to the cement to prevent rapid setting, regulate the primary, fast reactions, reduce drying shrinkage

Ettringite can react later on with water, go into solution and fill up later cracks, pores, voids (2-4 micron diameter needle like crystals can be formed, with 20-30 micron length).

In the cement system, the presence of ettringite depends on the ratio of calcium sulfate / tri-calcium aluminate (C_3A); when this ratio is low, ettringite forms during early hydration and then converts to the calcium aluminate monosulfate (or with C_3A to AFm phase (Al_2O_3-Fe_2O_3-mono)). When the ratio is intermediate, only a portion of the ettringite converts to calcium aluminate monosulfate and both can coexist, while ettringite is unlikely to convert to calcium aluminate monosulfate at high ratios.

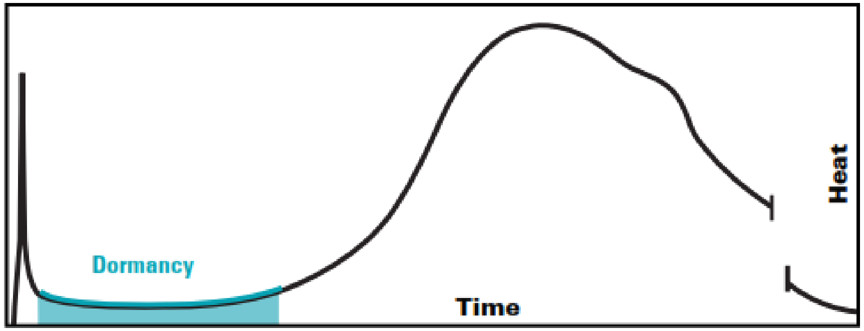
2. Inducing (dormancy)

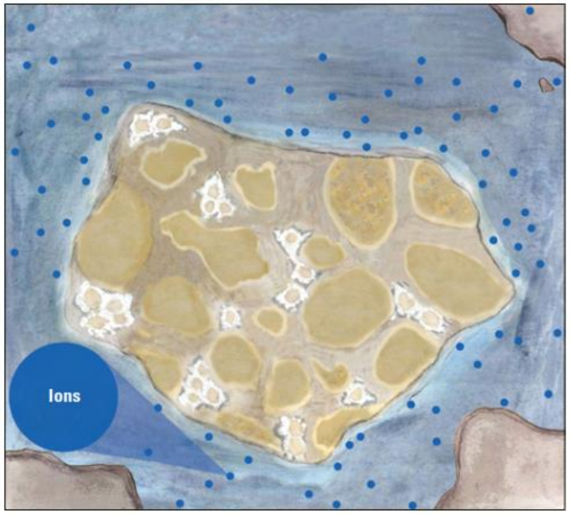
during 2-4 hours the **C-A-Ŝ-H** gels control the hydration

the solvation of the alite (C_3S) and belite (C_2S) continues slowly, the water becomes saturated with OH^- and Ca^{2+} ions

the concrete **does not generate heat**

the cement is still plastic, workable





3. Hardening

The **water becomes saturated** with Ca^{2+} ions (primarily from **alite**) and **hydrated compounds (CSH and CH)** start to form, the **stiffening** of the cement starts

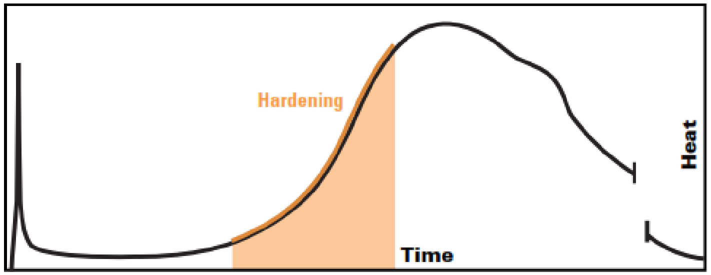
Hydration products continue growing, heat is generated, hydration process accelerates

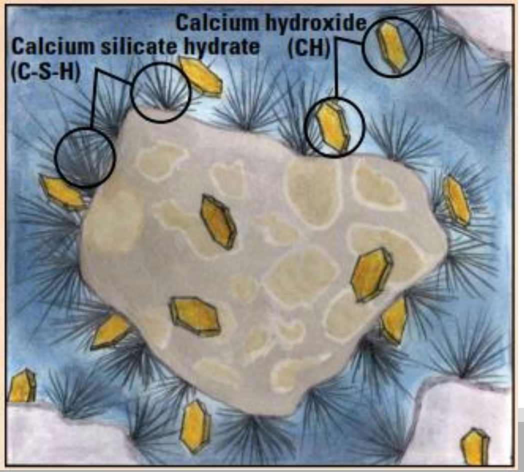
It lasts 2-4 hours. If the rate of reaction is slower, better microstructure can develop

Crystalline, fibrous hydration products will set around the grains forming a network

Aluminate and sulphate continue to react and a crystalline compound, the **ettringit** ($Ca_6Al_2[(OH)_{12}|(SO_4)_3]\cdot 26\ H_2O$) **(C-A-Ŝ-H)**

At the end of this stage the **concrete solidifys**, however cannot carry trafic. After this initial set **any forming of the cement should be finished**





4. Cooling

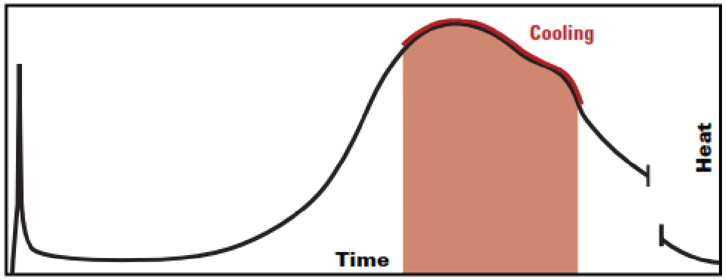
alite hydration slows, because CSH and CH sets up an obstacle between water and remaining cement grains

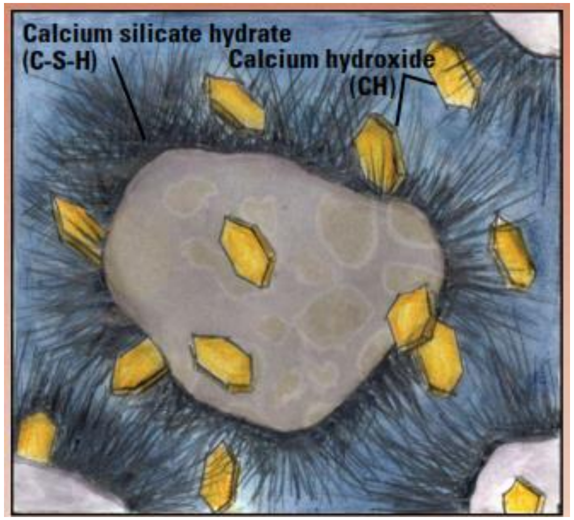
heat generation begins to drop

CSH and CH amount increases, strength increases

tensile strength and stress will increase, at some point stress will excedd strength and the concrete will crack. This can be controlled with joints

any remaining aluminate reacts with sulphate, **ettringite or monosulphate** is produced





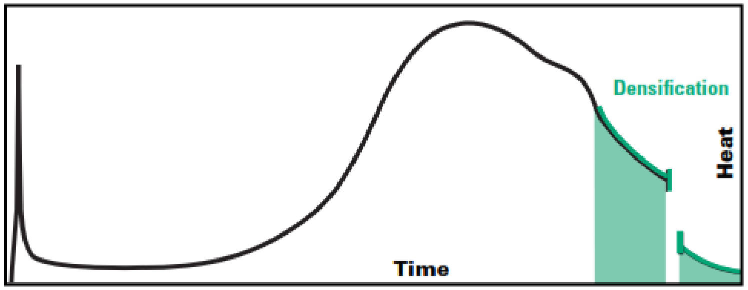
5. Densification

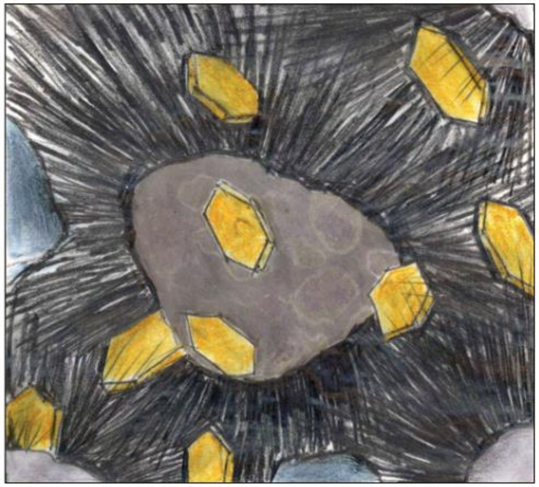
the **hydration continues slowly**, releasing small heat quantity

this process continues **untill water is present** in the concrete

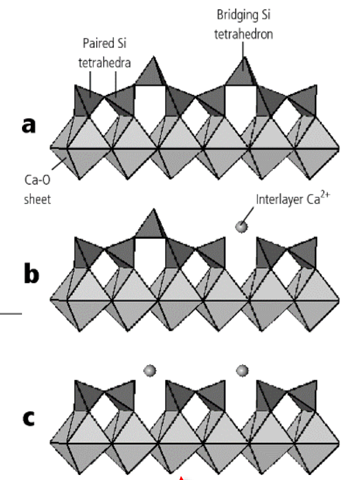
permeability has to be kept low. It can be reached by keeping concrete moist

- **alite will continue to hydrate untill water is present**. The volume of the hydration products grows, permeability (porosity) decreases, strength increases
- **belite reacts slower than alite**, even after several days its hydration continues if water is present





Hydration reactions

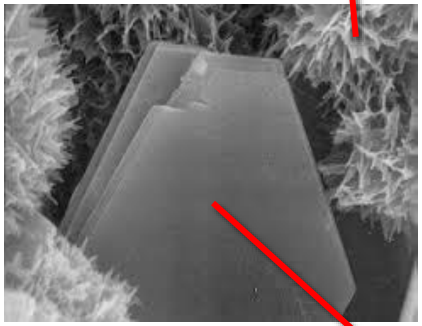


Alite (C_3S) reactions

$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$

$2C_3S + 7H \rightarrow C_3S_2H_8 + 3CH$

CSH-s are composed of crystallites, with sizes <1micron



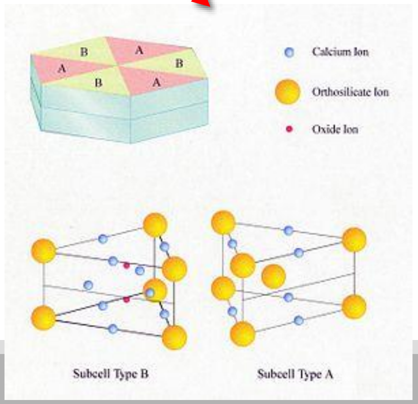
Belite (C_2S) reactions

$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$

Secondary hydration

$Ca(OH)_2$ **(portlandit),** hexagonal crystals

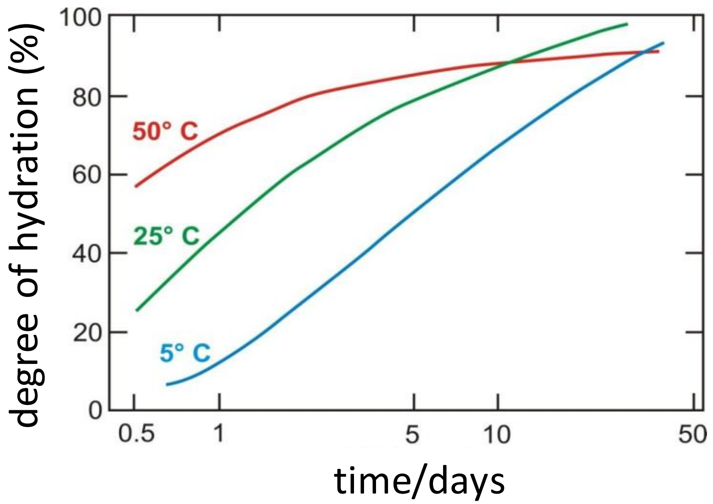
+ fresh water the **CH will leach out** (dissolve), increasing the porosity and thus making the paste more vulnerable to further leaching and chemical attack. CH is believed to play **a role in limiting the amount of shrinkage** that occurs when a cement paste is dried



Effect of temperature

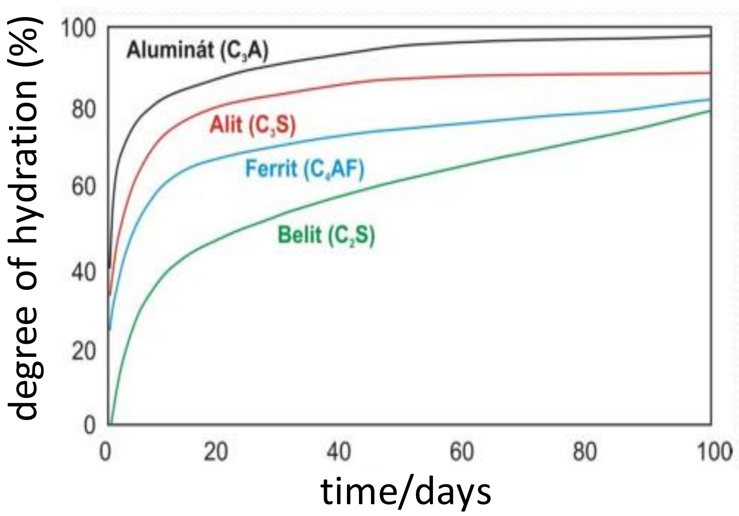
Alite hydration

- sensible to temperature only in the chemical controlled phases, in the last phase the temperature has no effect on it

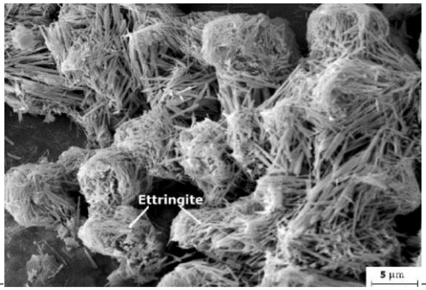


Belite hydration

- much slower
- it does not contribute to the initial strength
- small heat release



Hydration reactions



Tricalcium-aluminate

C_3A reacts with gypsum

$C_3A + 3C\hat{S}H_2 + 26H \rightarrow C_6A\hat{S}_3H_{32}$ (ettringit) exoterm

Ettringit is formed: $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$

- Ettringit in stable only if there is **enough sulphate** ion
- It will **coat the grains slowing down** its hydration

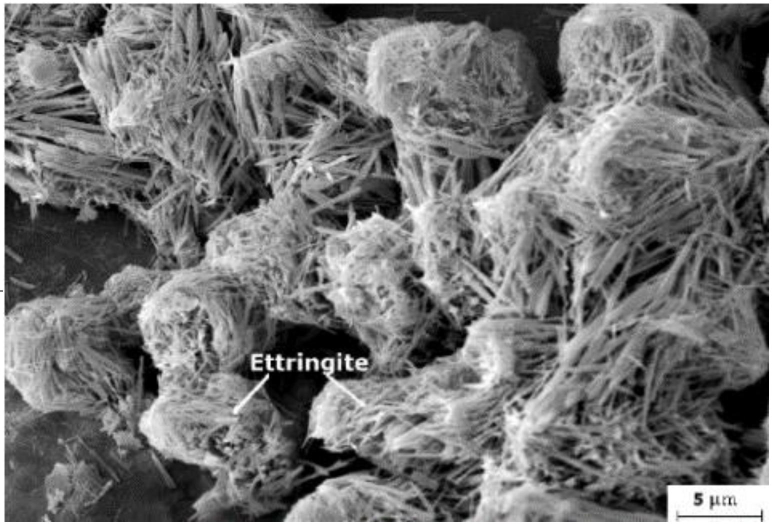
If there is no enough sulphate ion in the solution, the ettringite will transform is **calcium monosulphate**, that will break the hydrated layer covering the aluminate and fastening the the hydration of the aluminate.

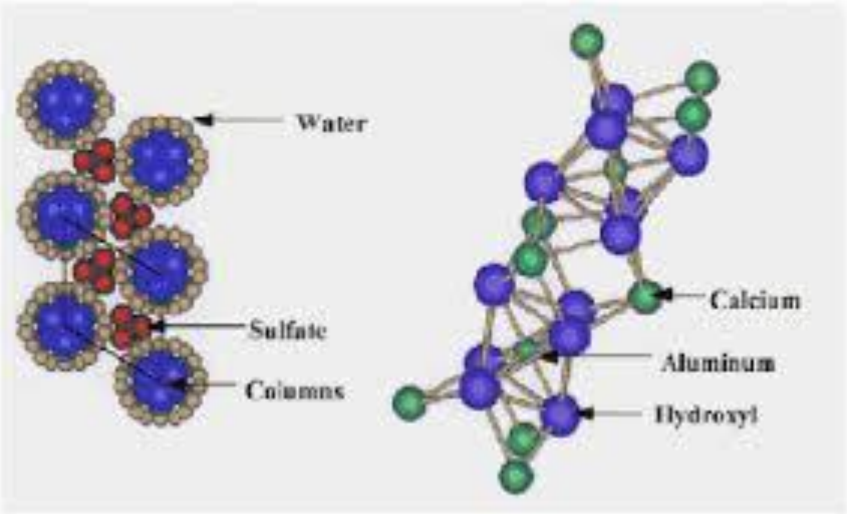
Fast aluminate hydration produces:
hydrogarnets **(C_3AH_6), $Ca_3Al_2(OH)_{12}$**

The later reaction of the **monosulphate** (**$C_4A\hat{S}H_{12}$**) with new sulphate ions (eg. from sulphate rains) will lead to the degradation of the concrete

- **$C_4A\hat{S}H_{12} + 2C\hat{S}H_2 + 16H \Rightarrow C_6A\hat{S}_3H_{32}$**

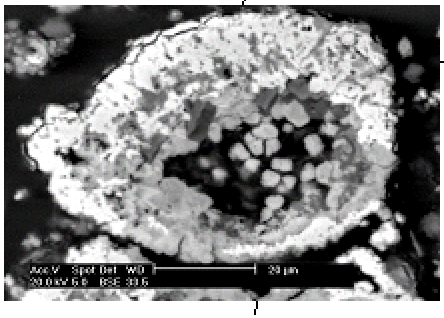
Ettringite

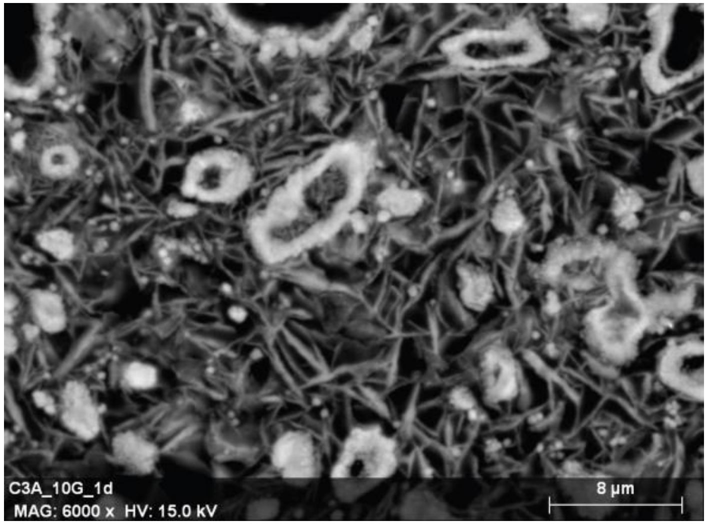

Ettringite
5 µm


Water
Sulfate
Columns
Calcium
Aluminum
Hydroxyl

C_3A hydration products

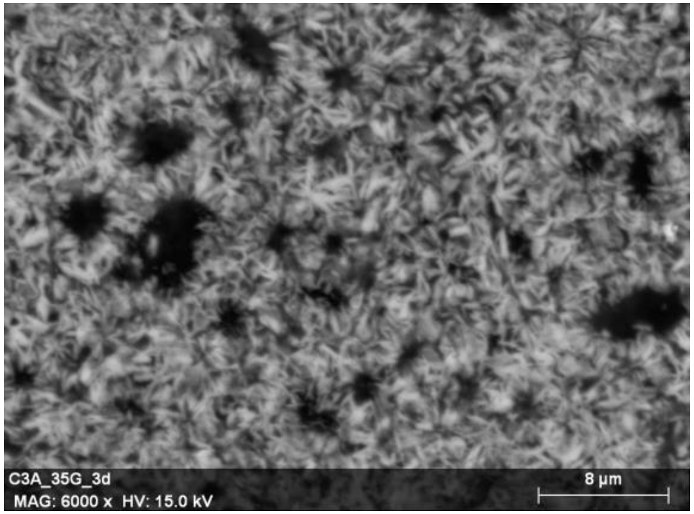
$C\hat{S}H_2/C_3A$ mole ratio	Hydration products
3	Ettringite
3-1	Ettringite + mono-sulpho-aluminate
1	Mono-sulpho-aluminate
<1	Mono-sulpho-aluminate solid
0	hydro garnets





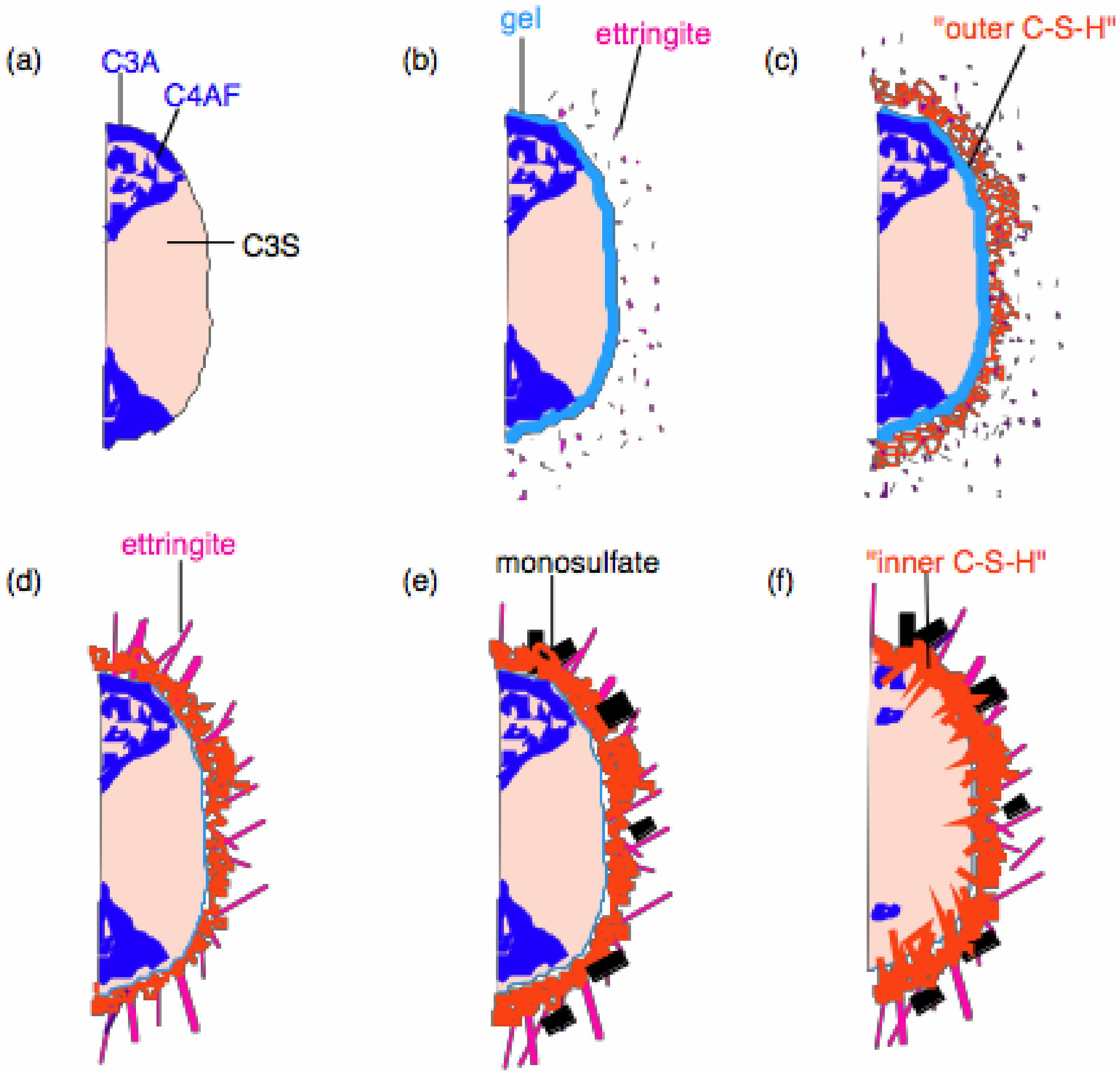
Hydrogarnets

(C_3AH_6), $Ca_3Al_2(OH)_{12}$



Monosulphate

($C_4A\hat{S}H_{12}$)



a) Hydration of the cement grain after

b) 10 minutes

c) 10 hours

d) 18 hours

e) 1-3 days

f) 14 days

C-S-H phases

Calcium-silicate-hydrates

CaO/SiO_2=1,5

Water content is very variable

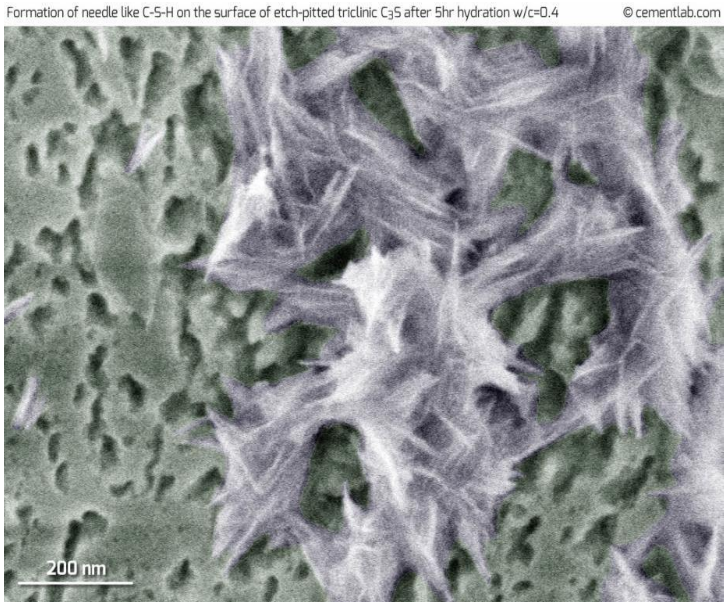
Structure: variable, from amorphous to crystalline phases

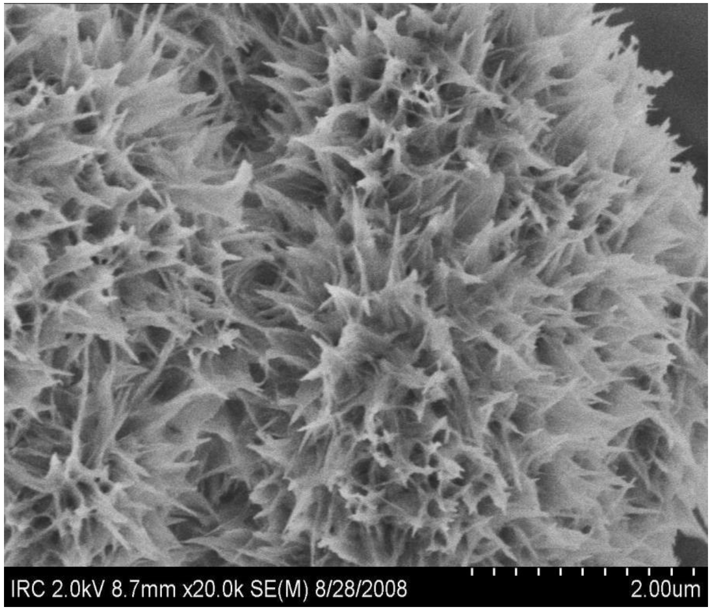
Bonding: 65%covalent, 35% van der Waals

50-60% of the hydrated cement paste

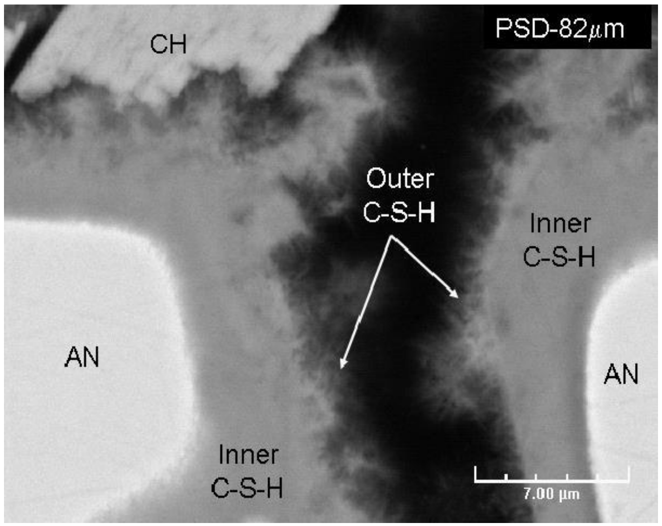
Great specific surface area

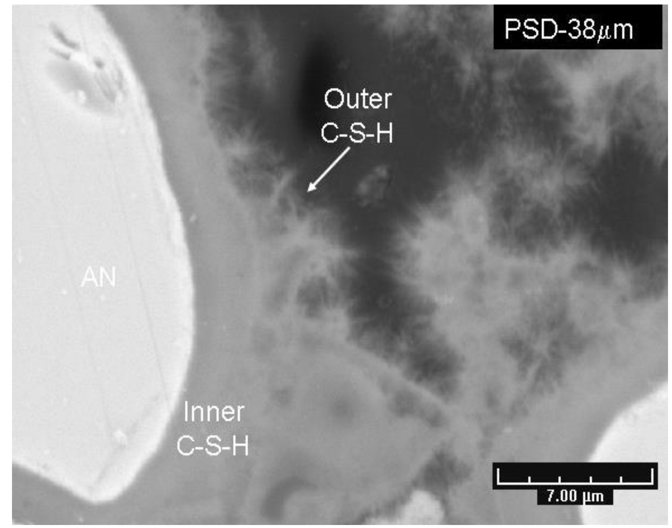
C-S-H phases

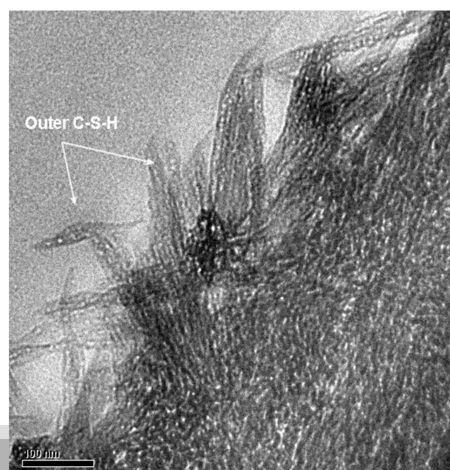

Formation of needle like C-S-H on the surface of etch-pitted triclinic C3S after 5hr hydration w/c=0.4
© cementlab.com
200 nm

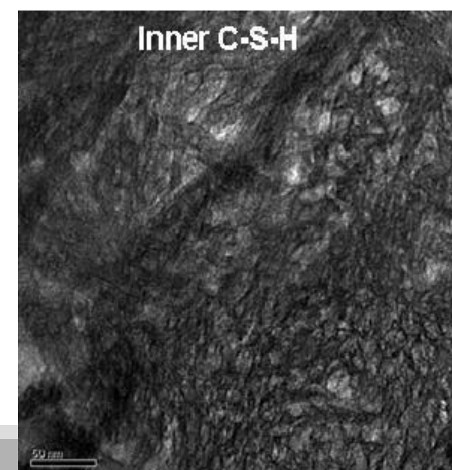

IRC 2.0kV 8.7mm x20.0k SE(M) 8/28/2008
2.00um

C-S-H phases

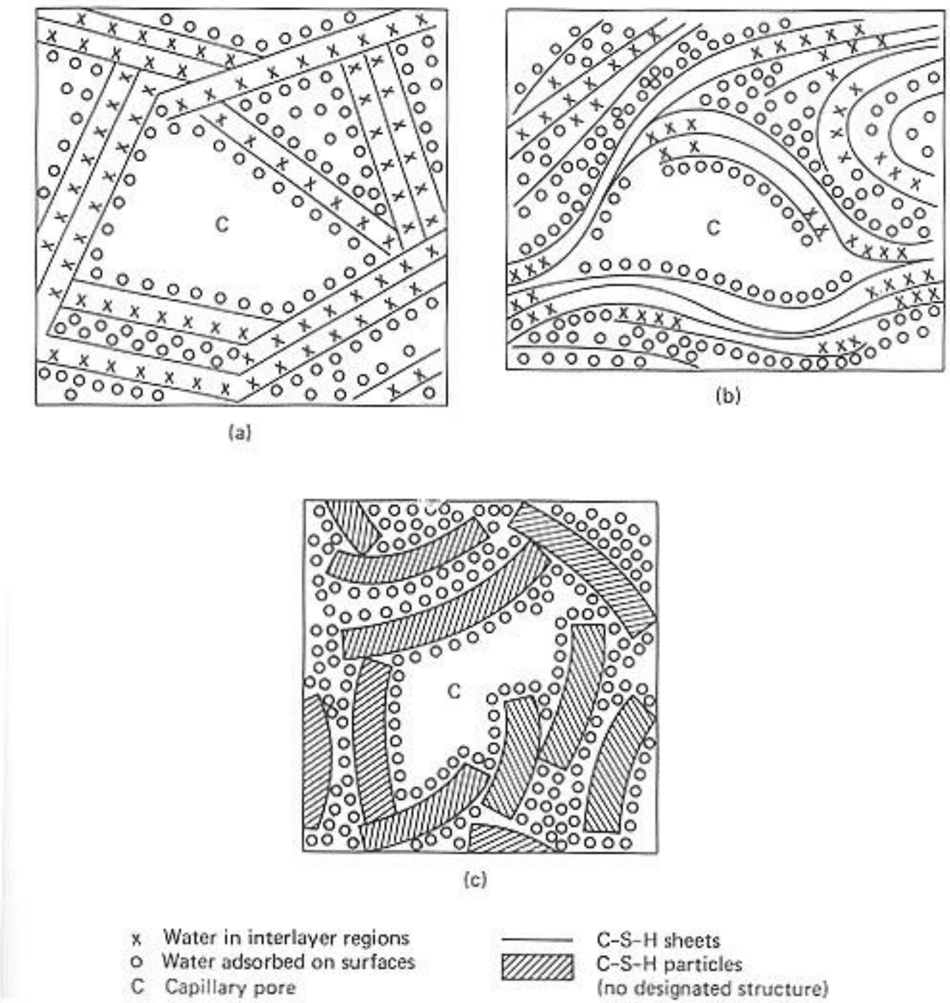

PSD-82µm
CH
Outer
C-S-H
Inner
C-S-H
AN
AN
Inner
C-S-H
7.00 µm

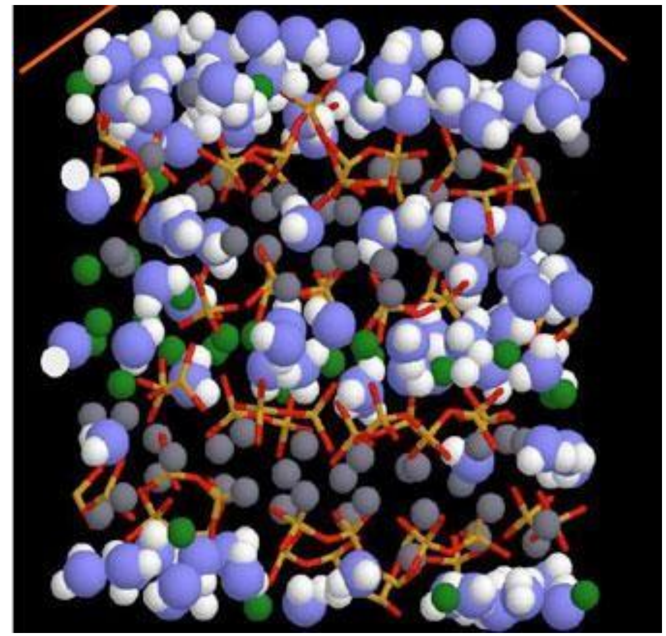

PSD-38µm
Outer
C-S-H
AN
Inner
C-S-H
7.00 µm


Outer C-S-H


Inner C-S-H

C-S-H structure





- blue-white: O and H atoms of water
- green – interlayer Ca
- grey – intralayer Ca
- yellow-red – SiO_2 tetraherdas

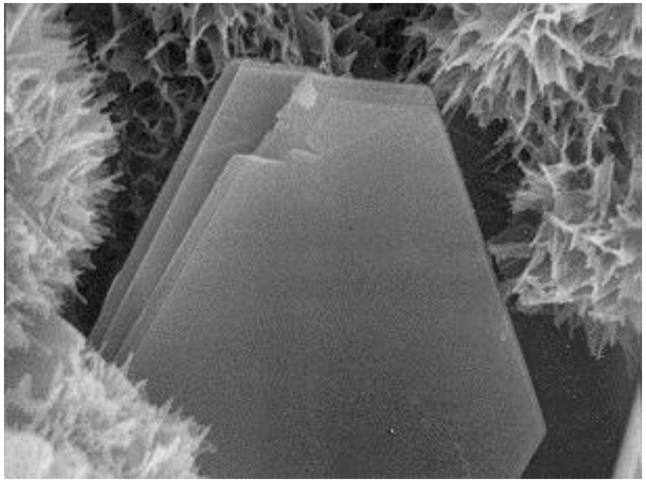
C-S-H structure

Portlandite (CH+H_2O)

hexagonal crystals

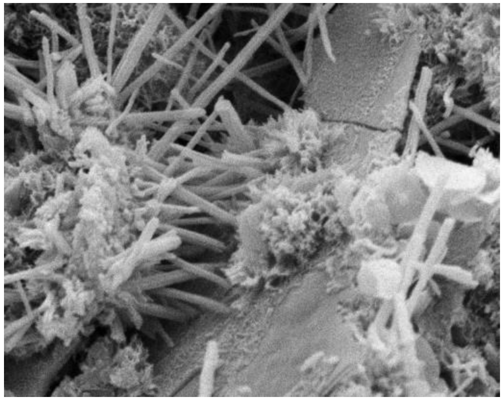
20-25% of the hydrated cement

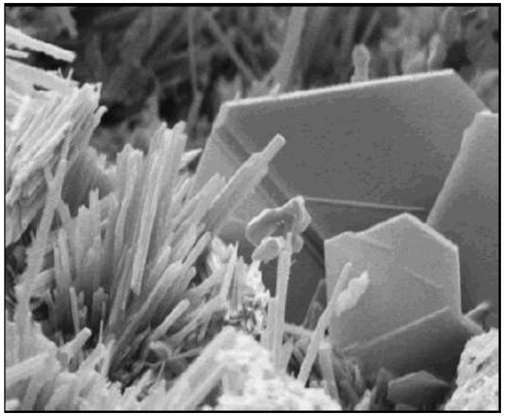
basic pH



Ettringite $C_6AS_3H_{32}$

$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$





LEGIT CIVIL ENGINEERING

presents