5ème Ecole d'automne du GDR MBS

Eco-conception des matériaux biosourcés et géosourcés : de la ressource à la fin de vie

12 au 16 octobre 2025, Douai

Approche physico-chimique de la décarbonation des matériaux à base de ciment Portland

Denis Damidot

IMT Nord Europe

Laboratoire de Génie Civil et géo-Environnement

IMT Nord Europe
École Mines-Télécom
IMT-Université de Lille

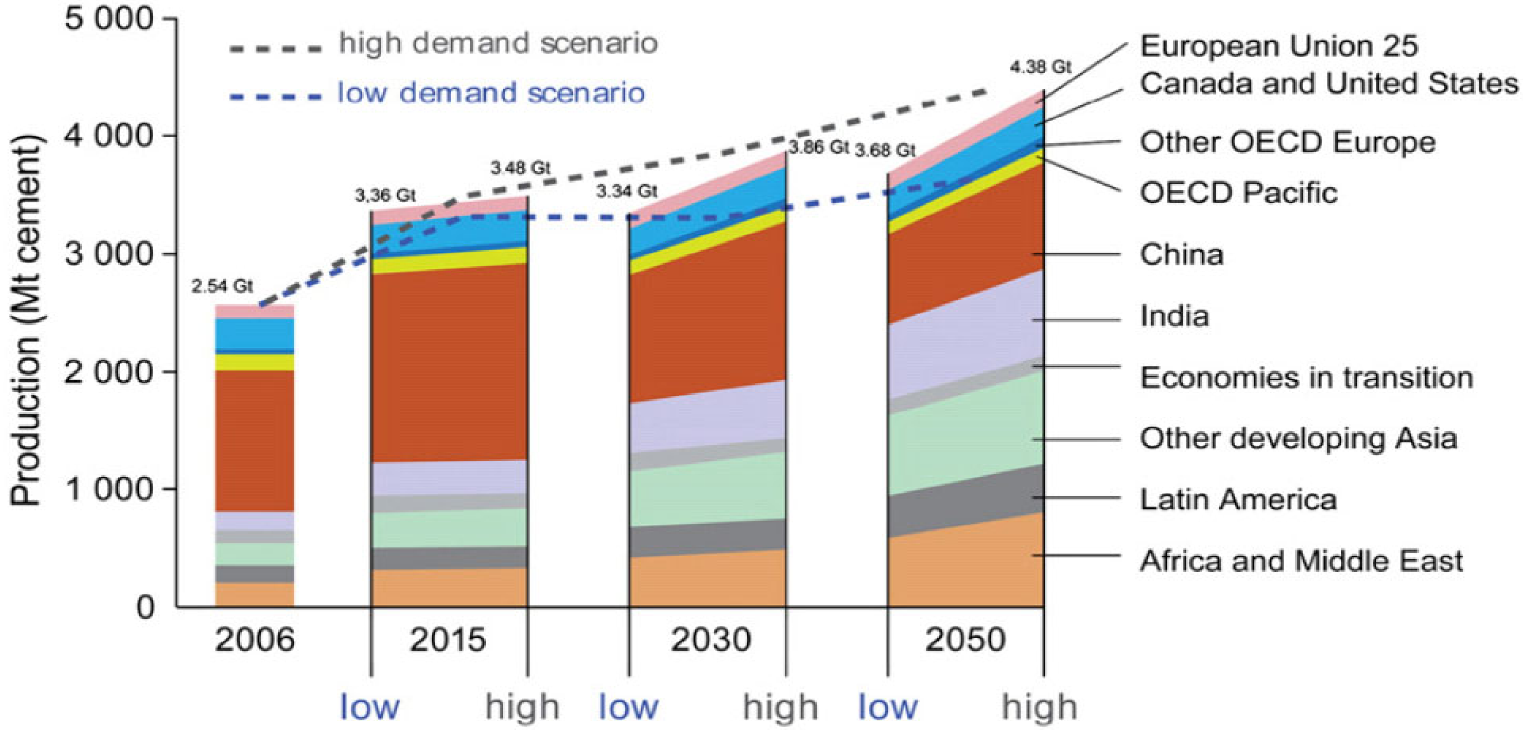
RÉPUBLIQUE FRANÇAISE

GdR MBS
MATÉRIAUX de CONSTRUCTION BIOSOURCÉS

cnrs

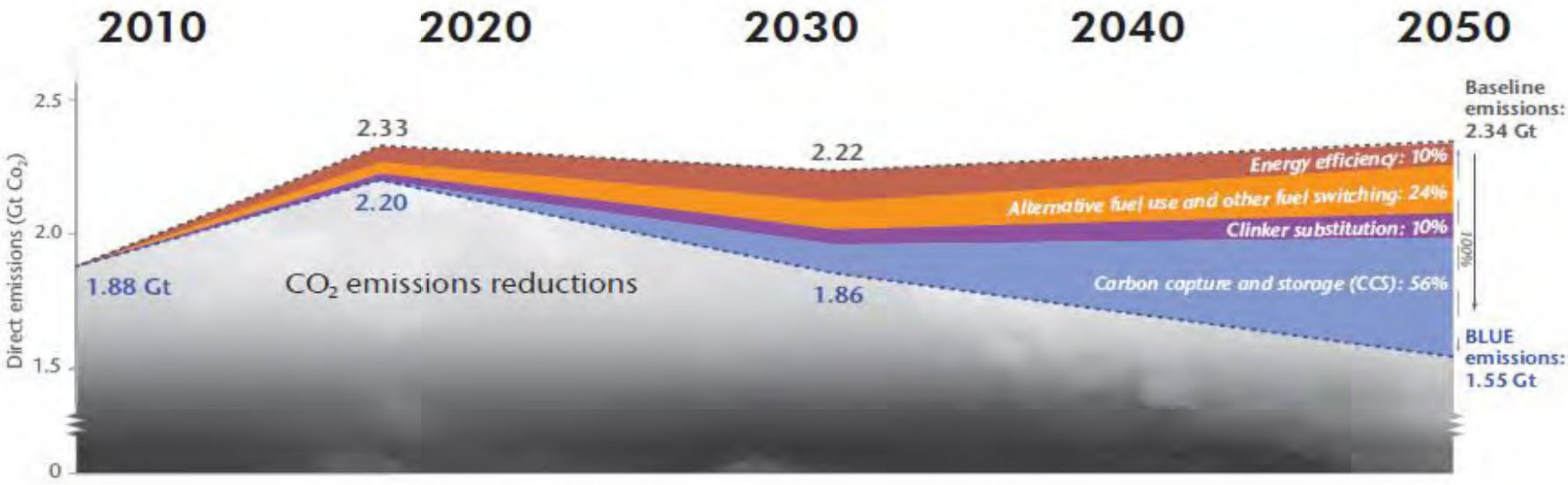
Concrete: a material forced to evolve to meet the challenges of sustainable development

1 – Raw material requirements: billions of tons of aggregates, cement, steel and drinking water and the expected doubling of needs by 2050



2 – About 8% of total CO_2 emissions per year for cement and 10% for concrete

Cement technology roadmap for CO_2 reduction

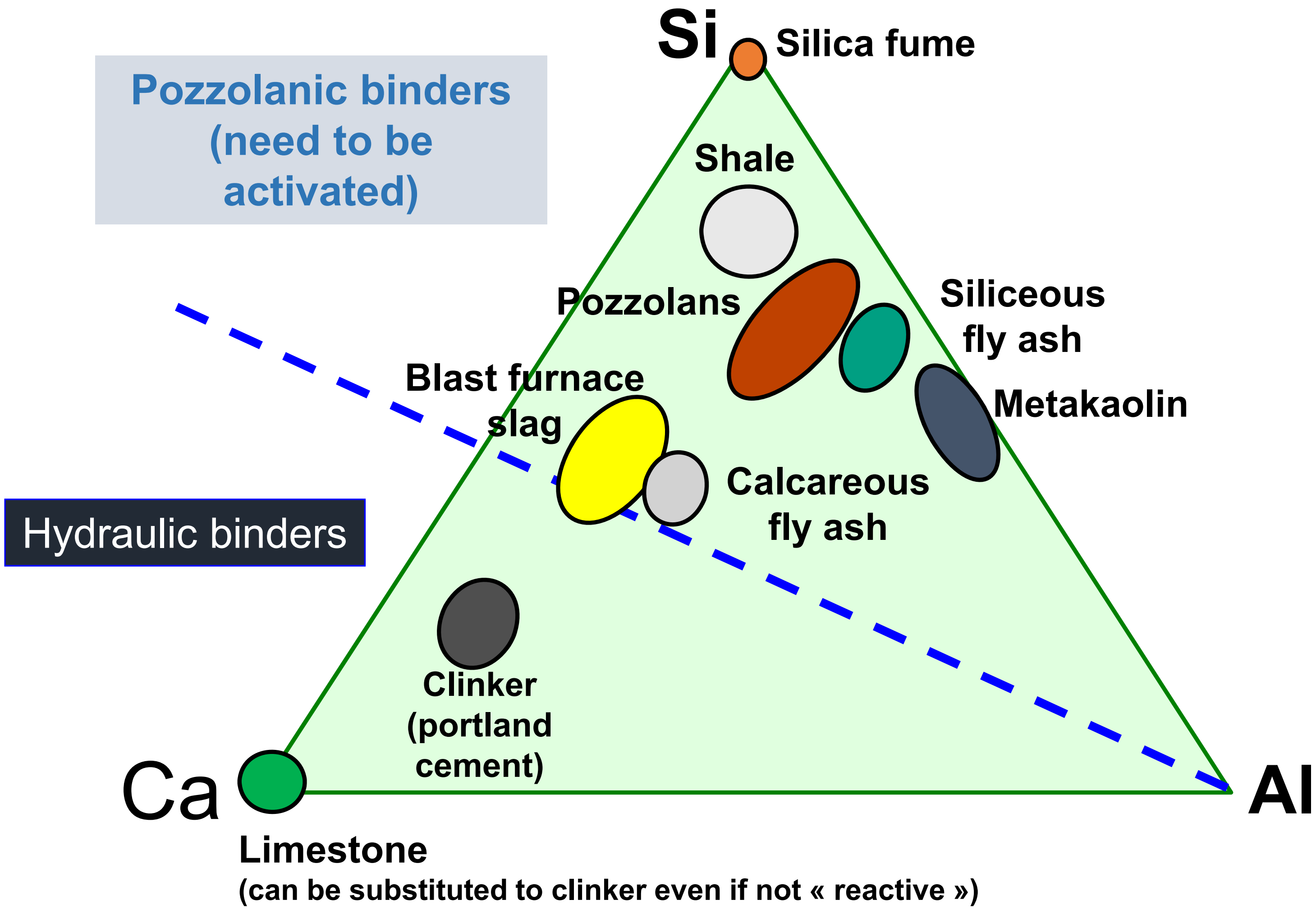


Source: IEA

Several technologies will be used concomitantly to reduce CO_2 emission despite a greater production of cement.

Approaches based on physico-chemistry mostly relies on clinker substitution by secondary cementitious materials (SCMs) but others possibilities exist.

Standard NF EN 197-1
Secondary cementitious materials (SCMs)



Chemical notation specific to cements using oxide formulas

$C = CaO$
$S = SiO_2$
$A = Al_2O_3$
$F = Fe_2O_3$
$M = MgO$
$H = H_2O$
$ or $\bar{S}$ or $\underline{S} = SO_3$
$\bar{C}$ or $\underline{C} = CO_2$

For example :

$C_3S = 3CaO.SiO_2 = Ca_3SiO_5$ = tricalcium silicate

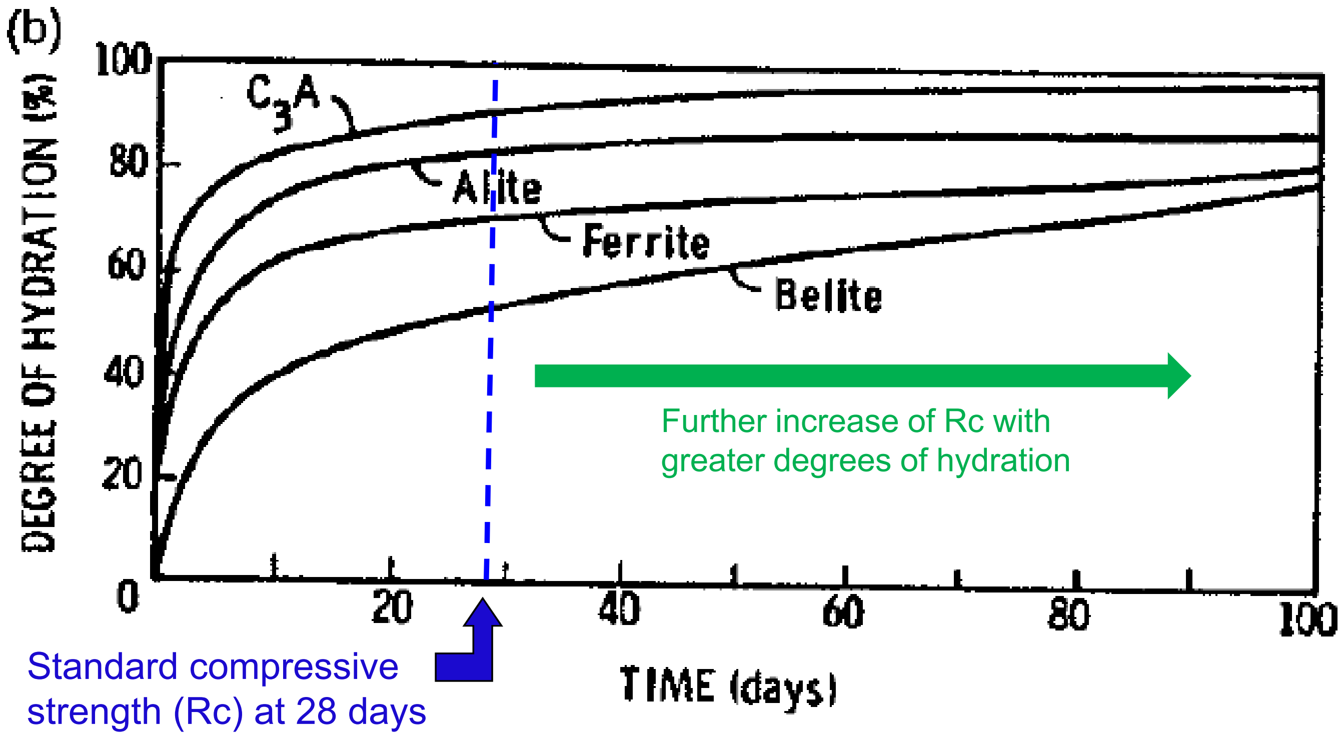
Possible answers to reduce CO_2 emissions of materials using cementitious materials thanks to physico-chemistry:

1 – use less limestone in raw materials:
- 1.1 alternative materials as a source of Ca
- 1.2 modified chemistry to obtain new binders leading to less emissions such as calcium sulfoaluminate cement

2 - reduce burning temperature:
- 2.1 use of mineraliser
- 2.2 increase reactivity with specific dopants for less reactive phases formed at lower temperatures
- 2.3 change the process: sol-gel methods at room temperature

3 – increase the reactivity of cement phases:

3.1 – reach higher percentages of hydration in less than 28 days :



Alite = C_3S
Ferrite = C_4AF
Belite = C_2S

Reactivity of the main phases of Portland cement

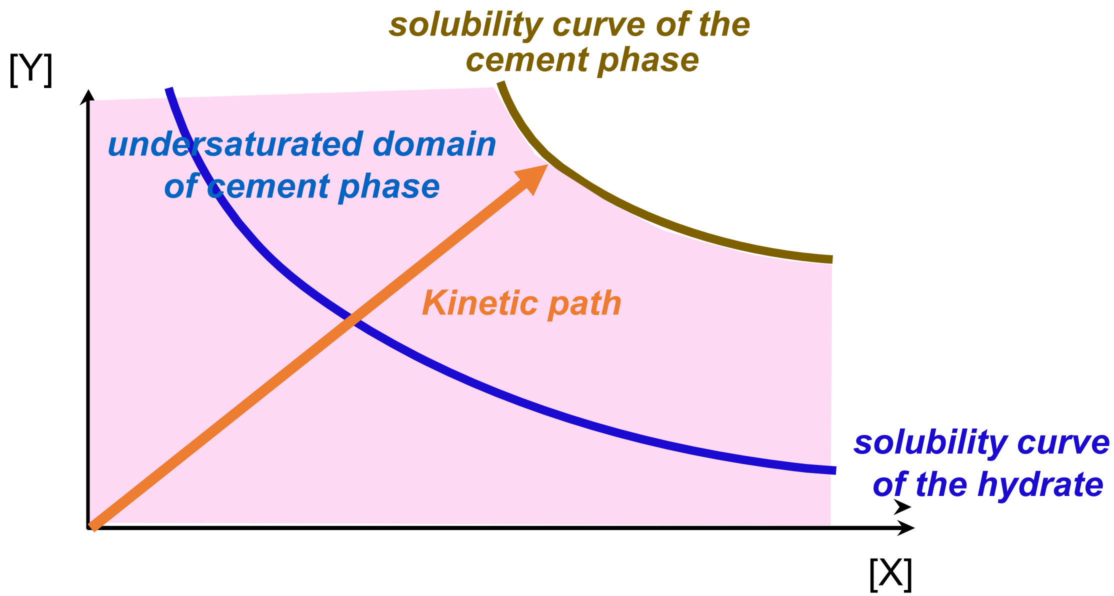
3 – increase the reactivity of cement :

- 3.1 – reach higher percentages of hydration in less than 28 days : need to increase reactivity of cement and SCMs
  - 3.1.1 – defects and / impurities or in crystal structure
  - 3.1.2 – increase specific surface area
  - 3.1.3 – dissolution enhancers
  - 3.1.4 – heterogeneous nucleation of hydrates on other surfaces than cement grains
- 3.2 – more efficient binders with « new » chemistry

4 – uptake of CO_2 by concrete: concrete that recarbonates

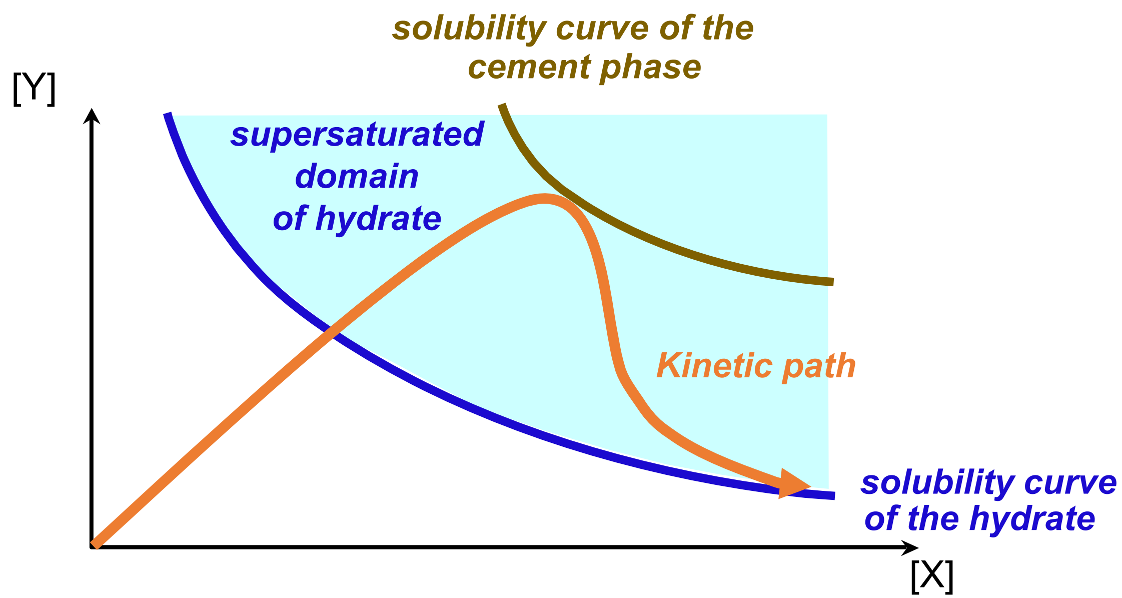
Competition between two equilibrium states is the driving force of cement hydration

equilibrium 1 : the cement that dissolves, tends to be in equilibrium with the aqueous phase



Competition between two equilibrium states is the driving force of cement hydration

equilibrium 2 : the aqueous phase has to be in equilibrium with the hydrate that precipitates



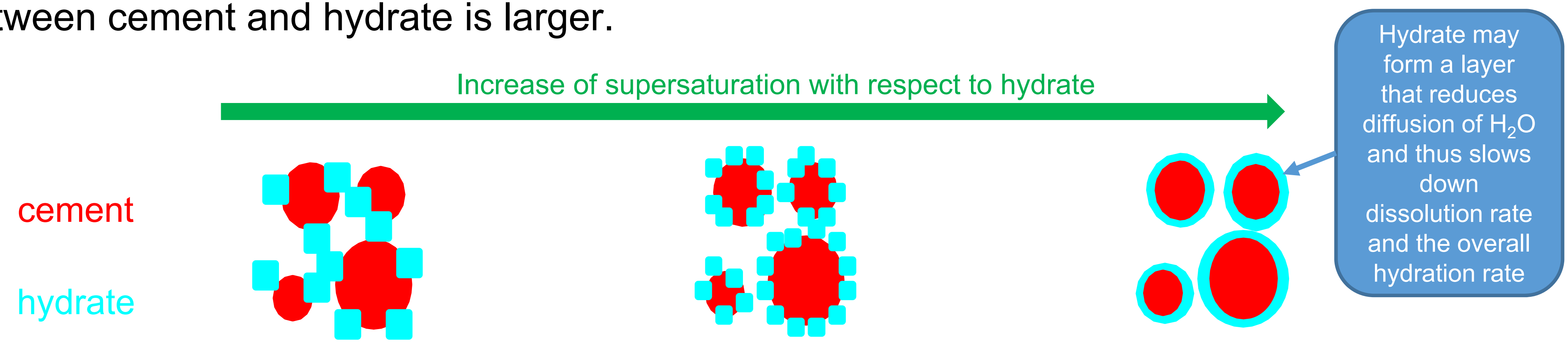
These two equilibrium conditions cannot be satisfied together : the solubility of the cement phase(s) that dissolves is higher than the solubility of the hydrate(s).
Thermodynamics indicates that the final state will be the more stable equilibrium : equilibrium 2

Competition between two equilibrium states is the driving force of cement hydration

The rate of hydration and the microstructure generated by hydration mainly depends on the difference of rates between dissolution and precipitation.

In pure water, dissolution rate of cement is high whereas precipitation rate varies with the value of the supersaturation of the aqueous phase with respect to the hydrate ; the higher the supersaturation level, the greater the nucleation rate.

Greater supersaturation values can be obtained when the difference of solubility between cement and hydrate is larger.

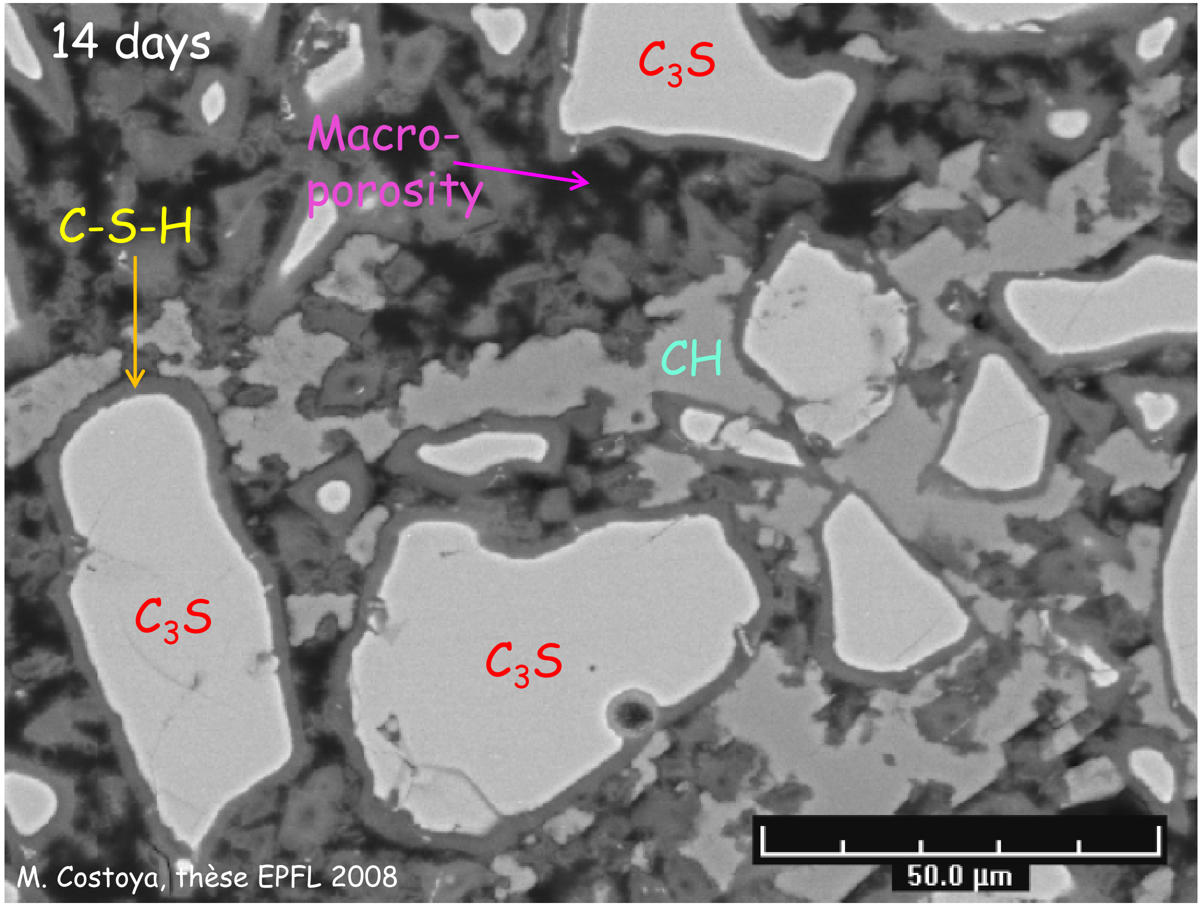


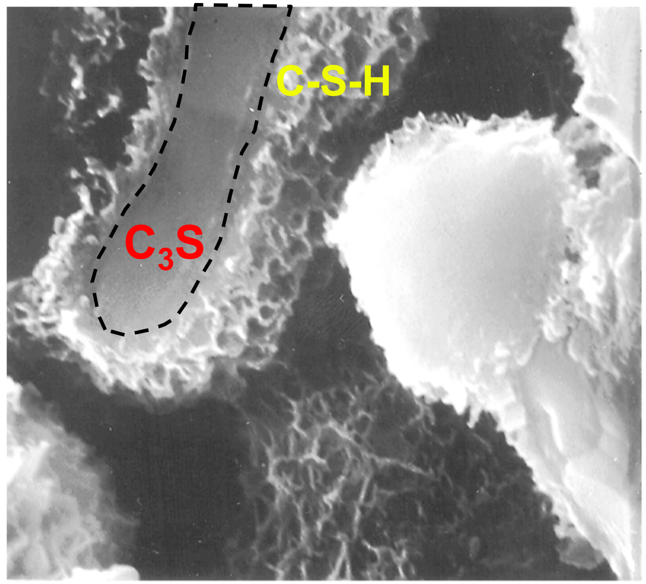
Weak nucleation
Strong growth

Strong nucleation
Weak growth

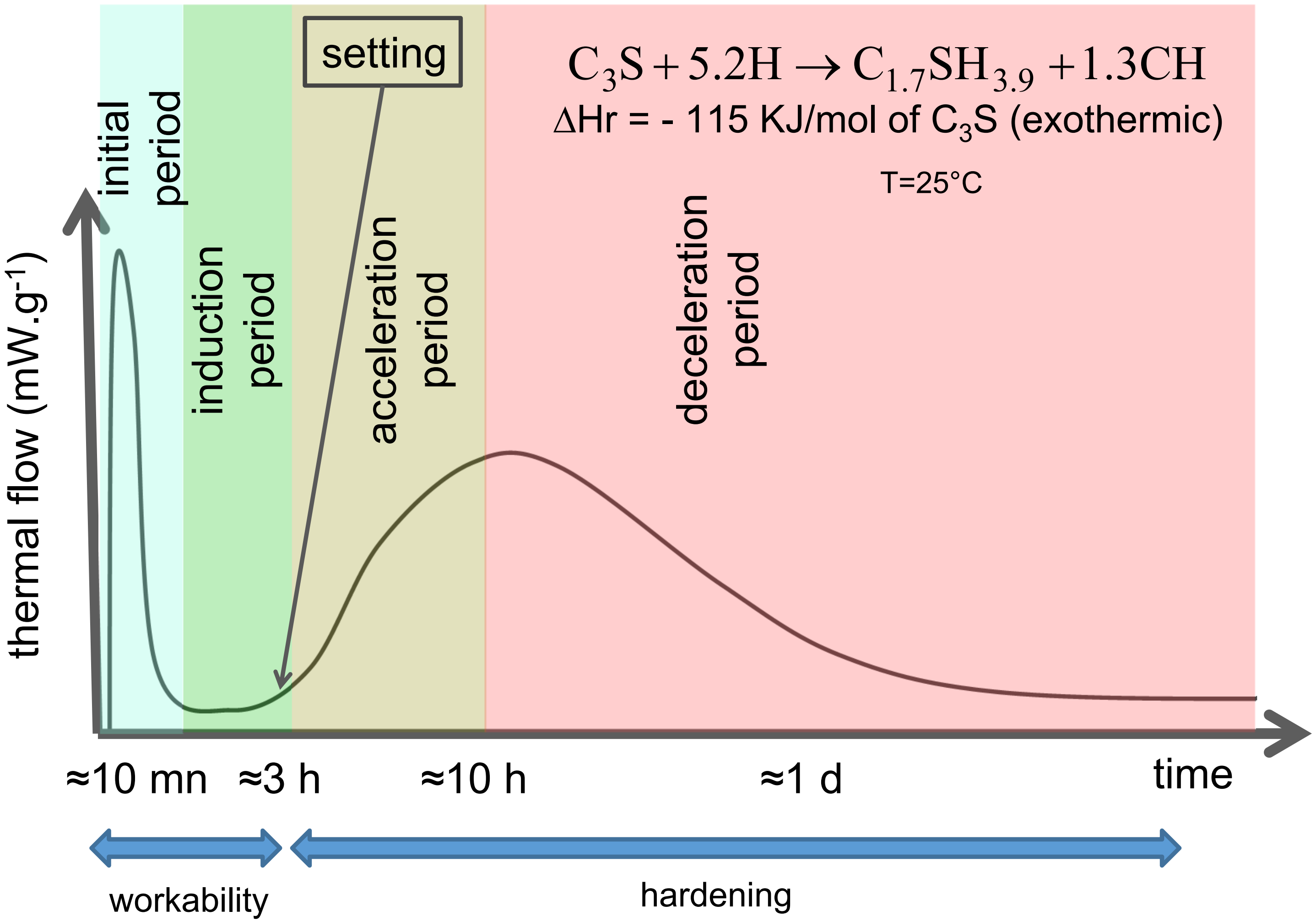
Very strong nucleation
Very weak growth

Tricalcium silicate (C_3S) hydration : hydrate rims formed by calcium silicate hydrate (C-S-H)



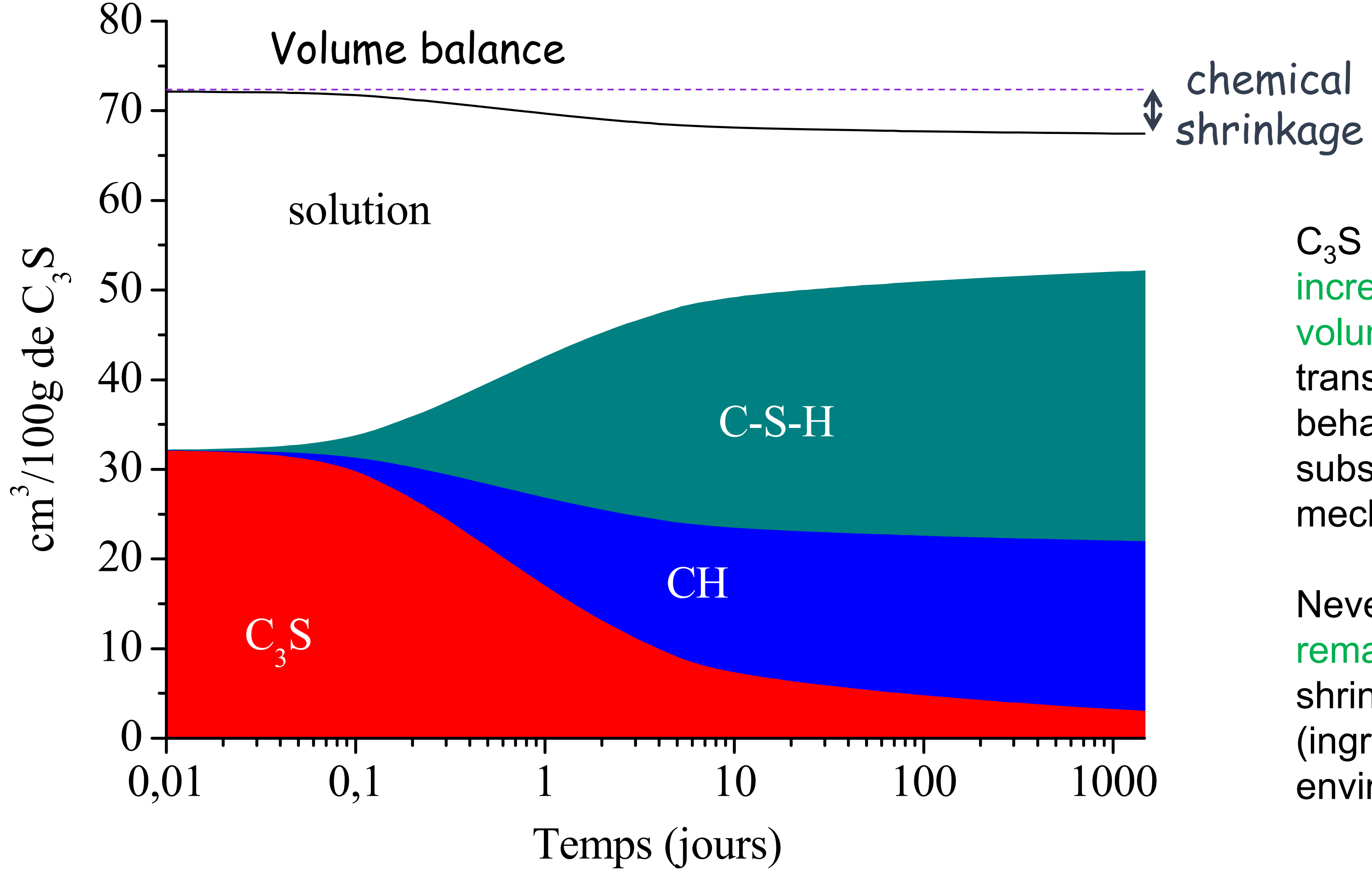


Tricalcium silicate (C_3S) hydration : kinetics



Decrease of hydration rate during induction period is due to a decrease of C_3S dissolution rate (induced by C-S-H layer on C_3S grains) and consequently a decrease of the rate of C-S-H nucleation and growth

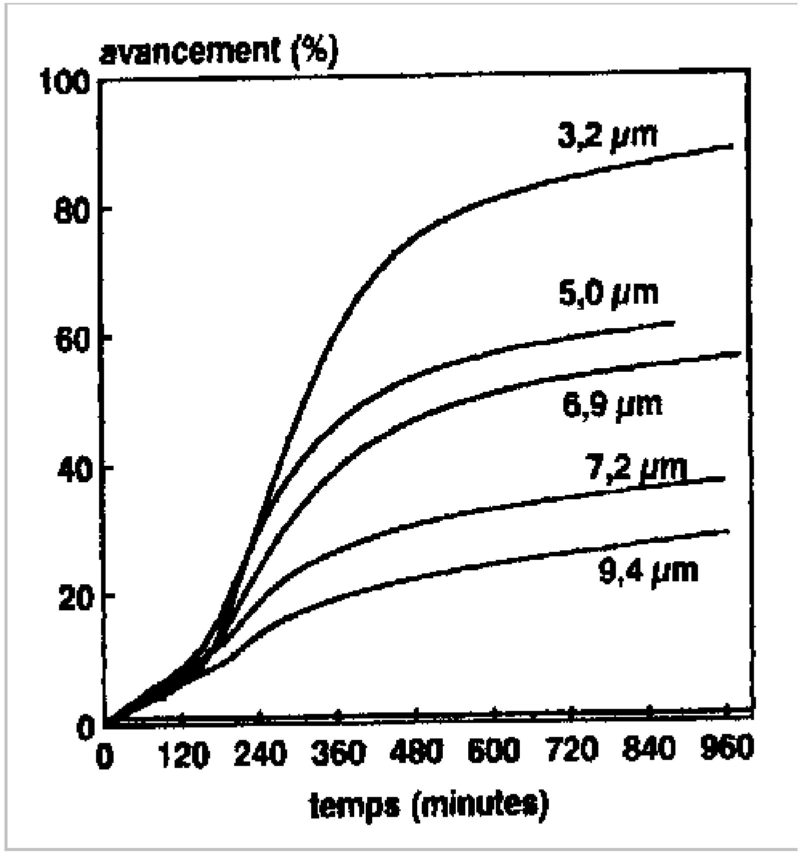
Tricalcium silicate (C_3S) hydration : volumic balance



C_3S hydration conducts to an increase of about 50% of the volume of solids leading to the transition from liquid to solid behavior (setting) and subsequently to the rise of the mechanical strength.

Nevertheless, porosity still remains leading to potential shrinkage and durability issues (ingress of chemical from the environment)

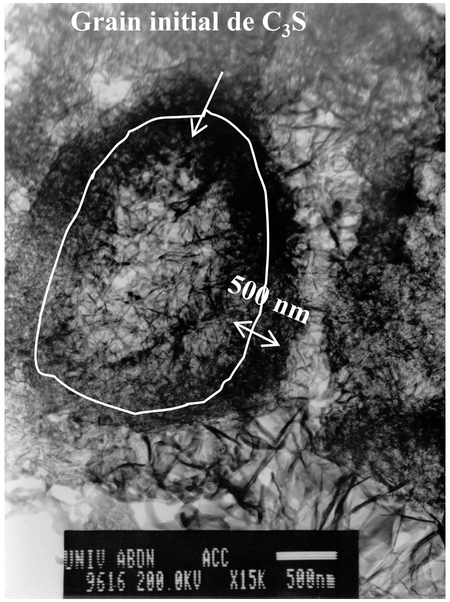
Tricalcium silicate (C_3S) hydration : effect of particle size



Percentage of reaction depending on d50 of C_3S powder

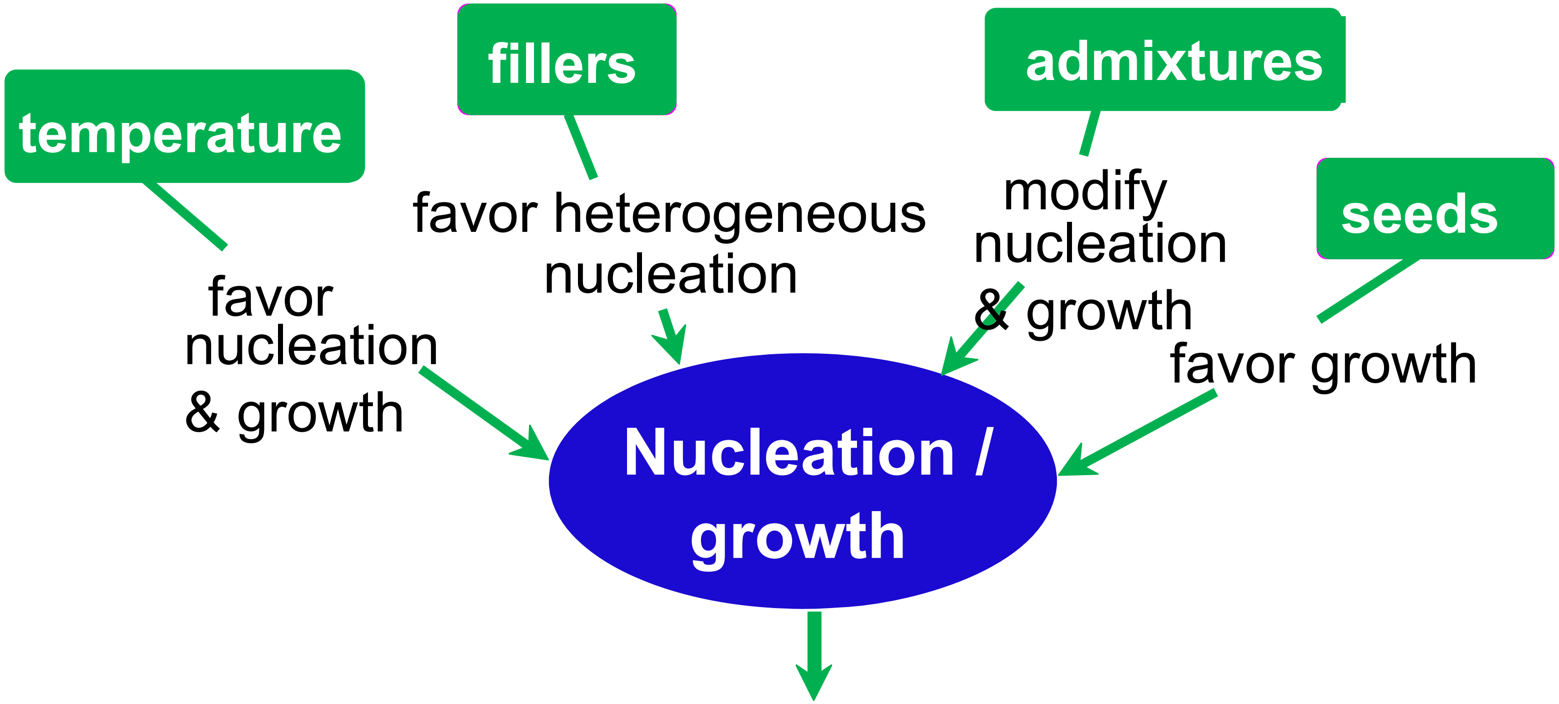
Smaller grains enable to reach greater percentages of reaction before getting a thickness of C-S-H layer that restricts C_3S dissolution rate.

It is estimated that C_3S grains having a diameter below 1.5 μm hydrates without being slowed by C-S-H layer ; critical thickness of C-S-H layer about 750 nm



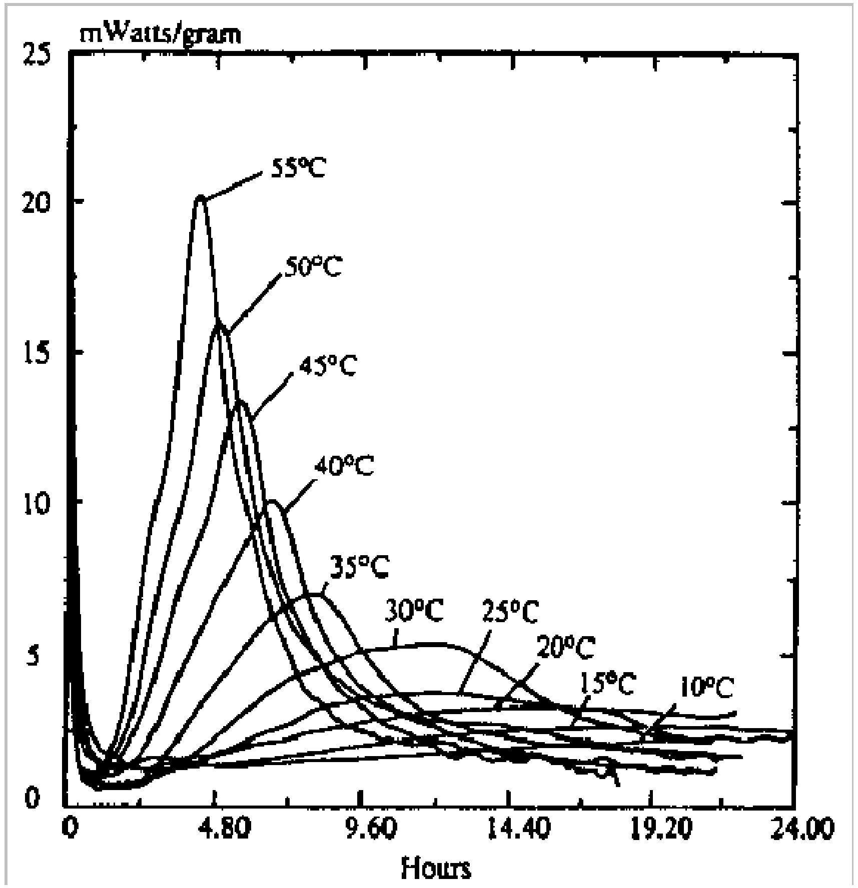
A greater finess of the cement is an efficient method to reduce the cement content without reducing the mechanical performance

Parameters impacting nucleation and growth



Localisation of hydrates, microstructure, rate of setting, shrinkage, mechanical strength, durability...

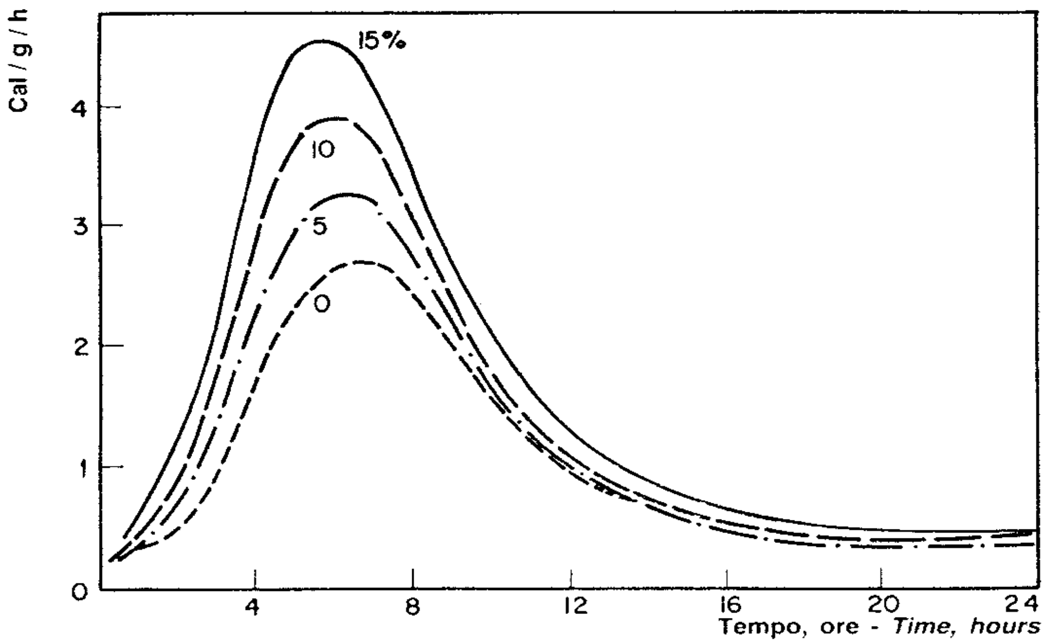
Tricalcium silicate (C_3S) hydration : effect of temperature



Temperature increases the overall C_3S hydration by several mechanisms ;

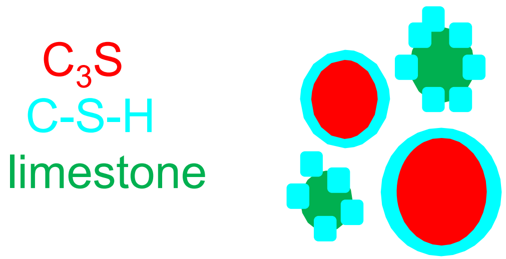
- increase of both C_3S dissolution and C-S-H nucleation rates,
- different growth of C-S-H (dominant 3D growth compared to 2D growth) leading to less effective layer in order to restrict water diffusion to further hydrate C_3S : thus greater percentages of reaction are reached.

Tricalcium silicate (C_3S) hydration : effect of fillers having a good affinity for C-S-H



Addition of limestone filler to C_3S

C-S-H is precipitated both on C_3S and limestone grains: thus the thickness of C-S-H layer leading to slowdown hydration rate is reached at higher values of the percentage of reaction.



For a cement having a partial substitution of clinker by limestone (up to 10 wt%), the higher percentage of reaction counteracts partially the decrease of clinker content with respect to mechanical strength.

Plaster ($CaSO_4.1/2H_2O$) hydration : effect of organic molecules

Usually a strong effect is observed in the presence of (water soluble) organic molecules (that may be released by bio-based constituents); very often organic molecules slow down both dissolution and nucleation. Moreover the crystal shape associated with growth can be markedly modified.

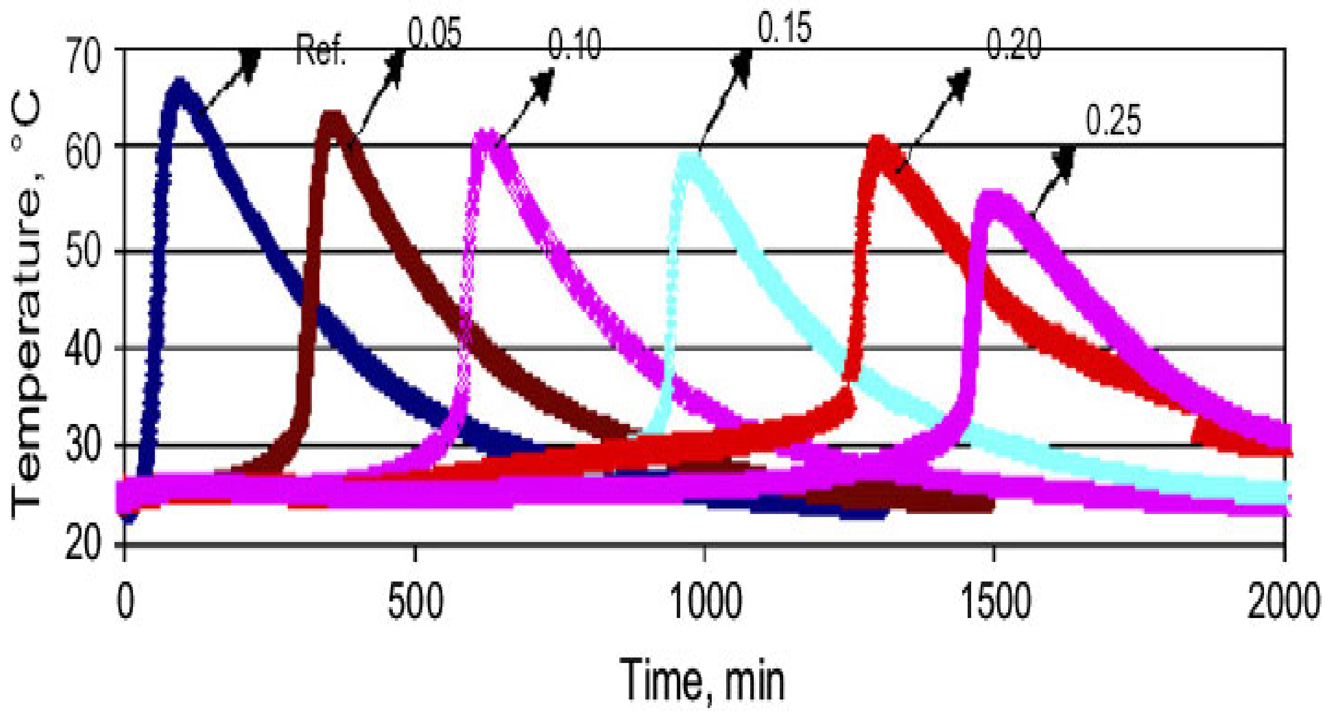
Plaster hydration is used as gypsum (that is the product of plaster hydration) forms large crystal easily observable :

$$\boxed{CaSO_4.\tfrac{1}{2}H_2O + 1.5H_2O = CaSO_4.2H_2O}$$

$$\boxed{0{,}67V_{semi} + 0{,}33V_{H_2O} = 0{,}93V_{gypse}}$$

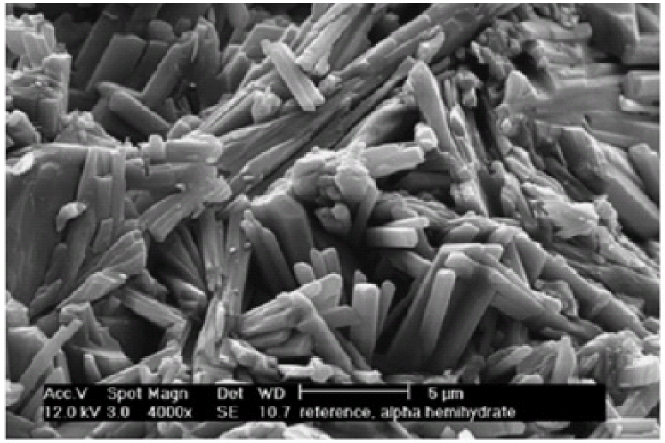
Volume total ↓ 7% *mais* Volume solide ↑ x1.4

Plaster ($CaSO_4$.1/2H_2O) hydration : effect of malic acid

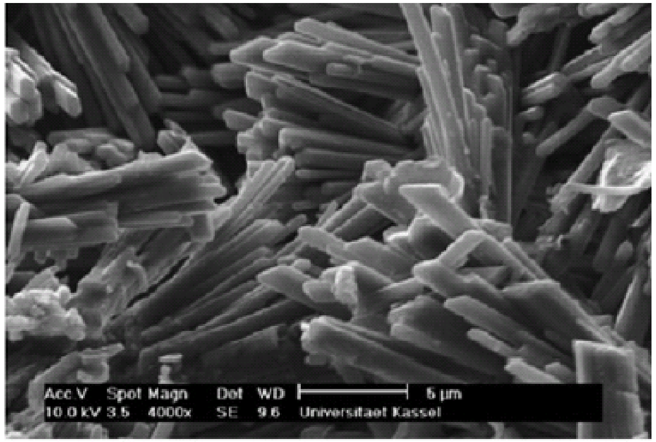


Effect of malic acid (wt%) on plaster hydration (w/p=0.35)

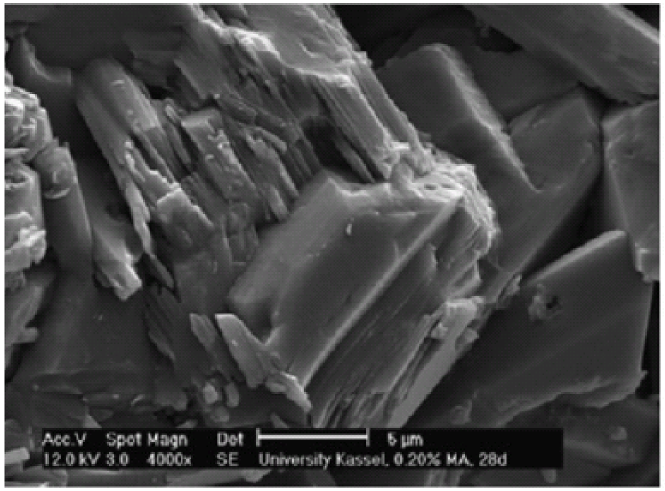
Plaster ($CaSO_4.1/2H_2O$) hydration : effect of malic acid



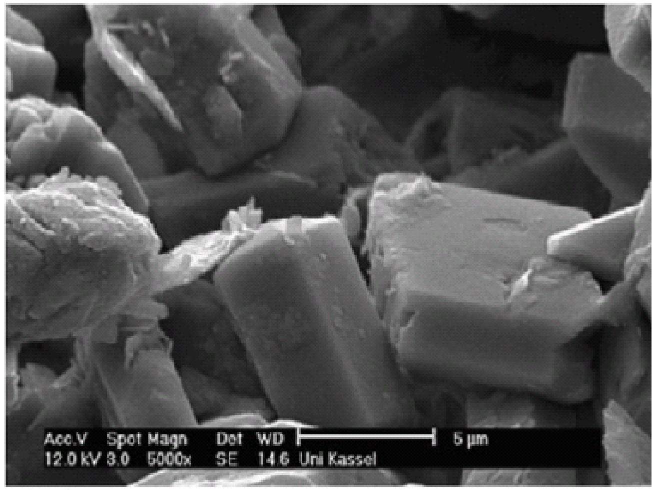
(a) α-hemihydrate-reference



(e) β-hemihydrate-reference

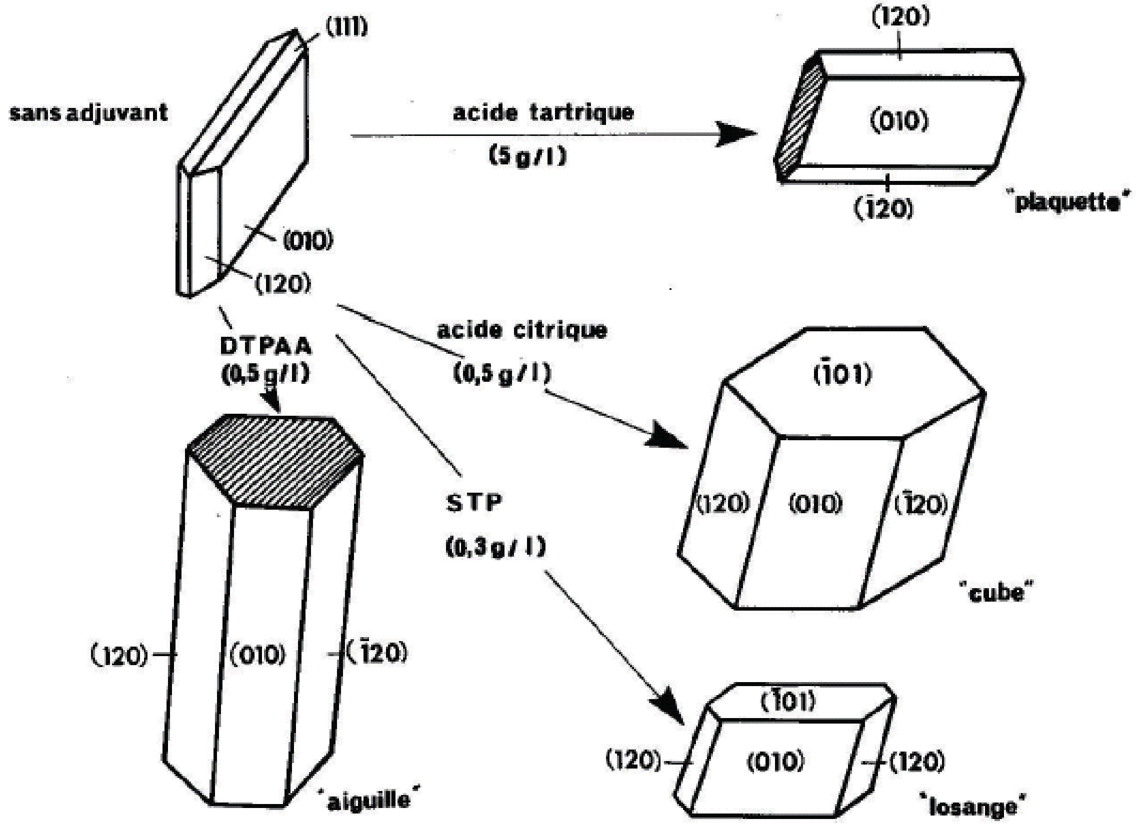


(b) α-hemihydrate (0.2 wt% malic acid)



(f) β-hemihydrate (0.2 wt% malic acid)

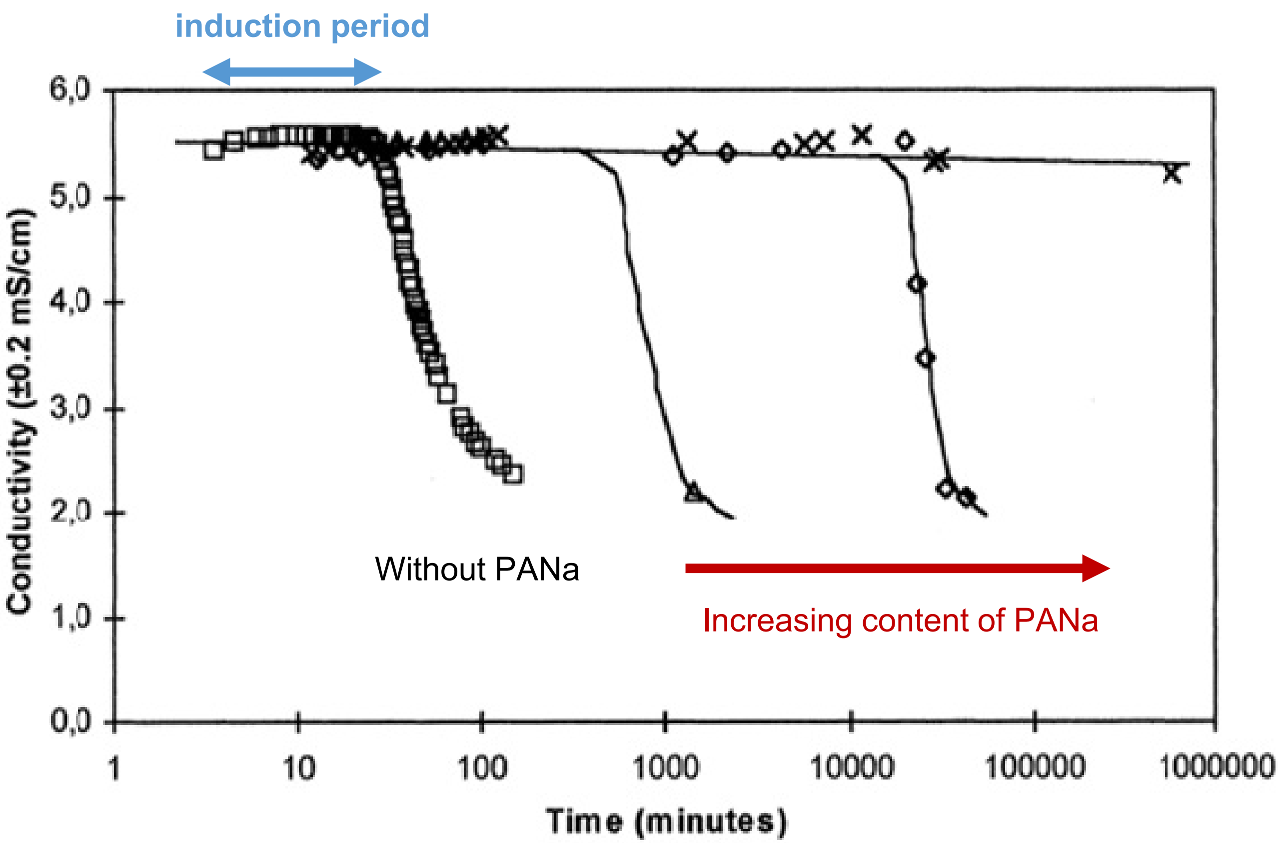
Effect of organic molecules on gypsum growth



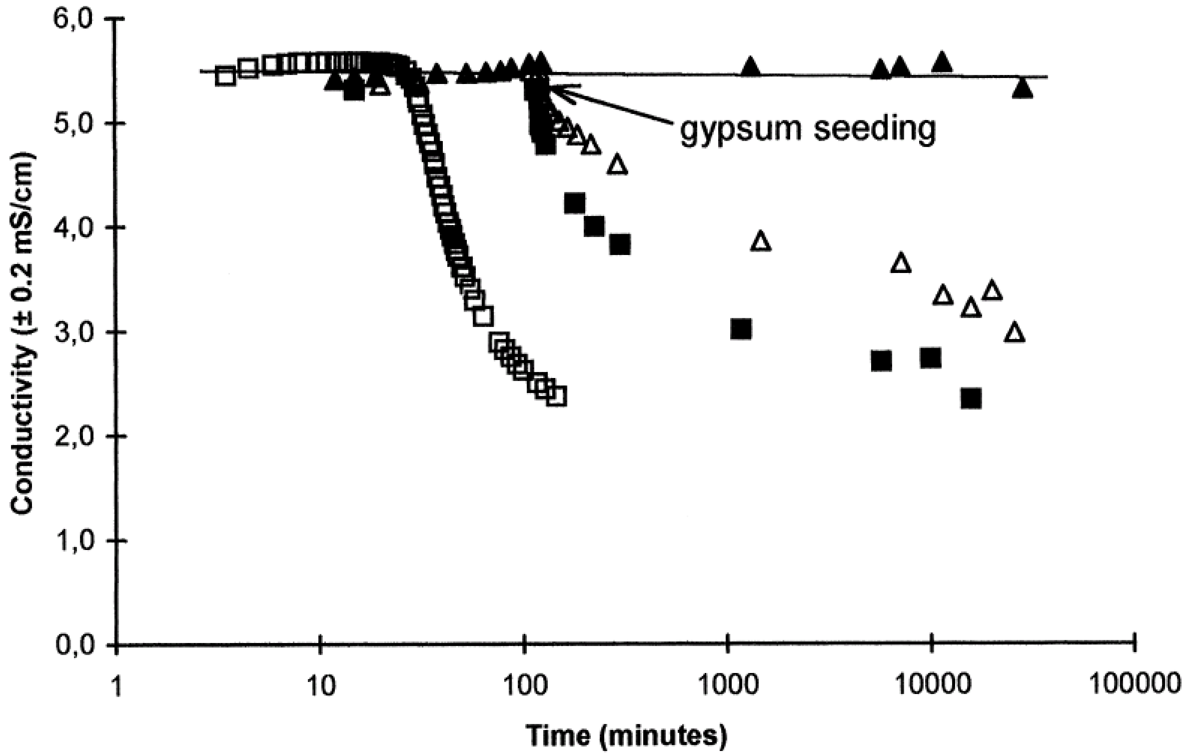
Crystallographic facies as a function of different organic molecules

Plaster ($CaSO_4.1/2H_2O$) hydration : retardation of nucleation

Retarding effect of sodium polyacrylate (PANa) on nucleation of gypsum when added to a supersaturated solution with respect to gypsum.

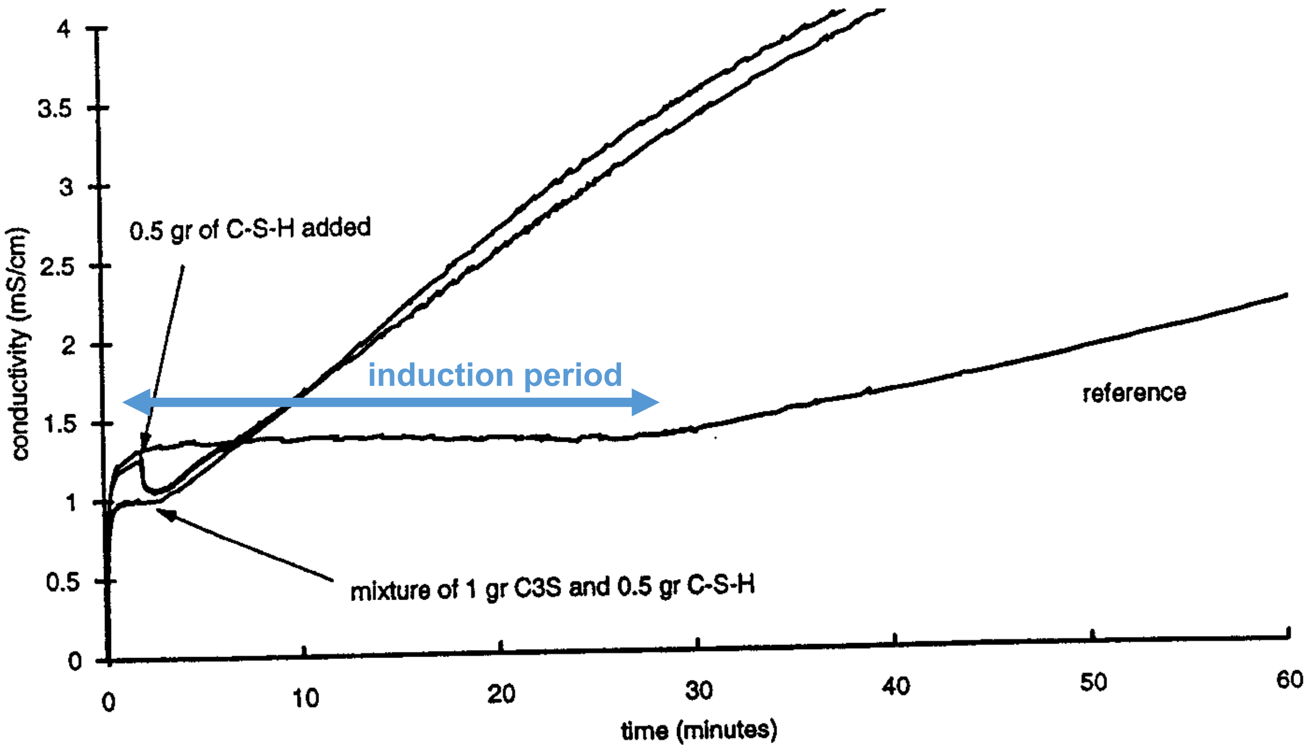


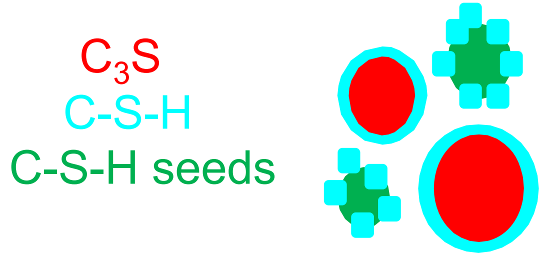
Plaster ($CaSO_4.1/2H_2O$) hydration : effect on gypsum seeds on the retardation of nucleation induced by PANa



Addition of seeds (same mineral as the mineral that should precipitate) is a very effective method to speed up nucleation and promote growth ; in the present case, the induction period ends immediately when seeds are added.

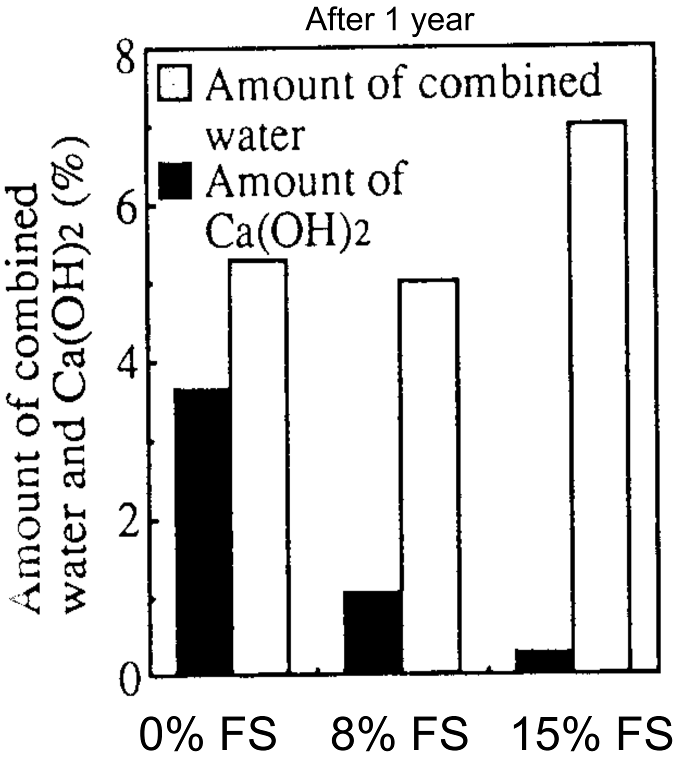
Tricalcium silicate (C_3S) hydration : effect of C-S-H seeds

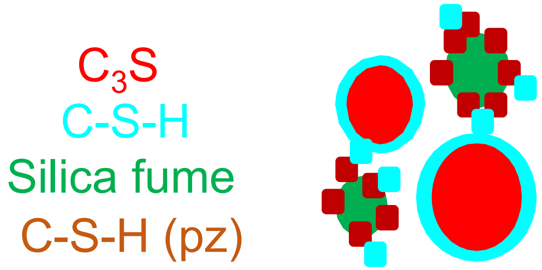




The addition of C-S-H either in the raw mix or during the induction period, reduces or suppress the induction period during early hydration that is governed by C-S-H nucleation.
Moreover, C-S-H is precipitated both on C_3S and C-S-H seeds : thus the thickness of C-S-H layer leading to slow C_3S dissolution is reached at higher values of the percentage of reaction : some commercial admixtures are containing C-S-H seeds.

Tricalcium silicate (C_3S) hydration : effect of pozzolanic filler





Case of silica fume (very fine particles of SiO_2 recovered from gases generated by the silicon industry):

Silica fume reacts with calcium hydroxide to form additional hydrated calcium silicate (pozzolanic reaction) :

$$Ca(OH)_2 + SiO_2 \Rightarrow \text{C-S-H (pz)}$$

With regard to mechanical strength (in the short and medium terms), the reduction in the quantity of clinker is compensated by:

- a greater quantity of C-S-H formed (C-S-H from the clinker + C-S-H pz)
- C-S-H pz which can serve as seeds for the growth of C-S-H, leading to greater hydration progress before the slowdown in water diffusion through the C-S-H layer

Conclusion et perspectives

The physicochemical approach is one way to reduce the environmental footprint of Portland cement-based building materials.

The current strategy, mostly based on reducing the amount of clinker through substitution, can be further optimized through better control of the dissolution and precipitation reactions that govern cement hydration. Furthermore, systematically increasing the fineness of the cement and the substitution constituents allows this strategy to be taken even further.

Construction materials using bio-based constituents are good candidates for implementing this strategy of reducing the quantity of clinker, leading to materials with a reduced carbon impact.

However, some attention has to be paid on the possible effect of organic molecules released by bio-based constituents on both dissolution and precipitation rates. On the other hand, some bio-based constituents can be efficient surface for the nucleation of C-S-H and thus can act as filler.