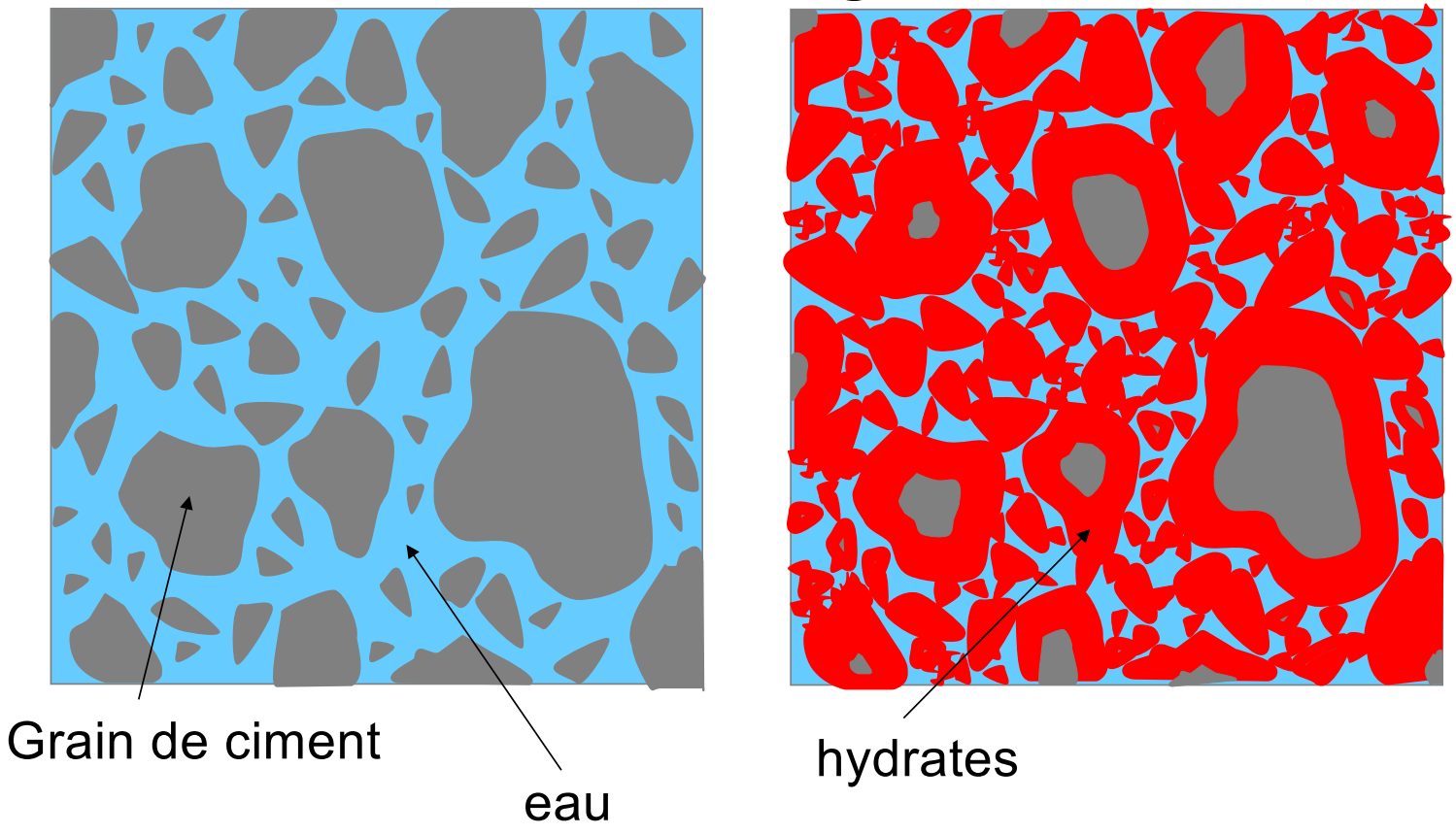
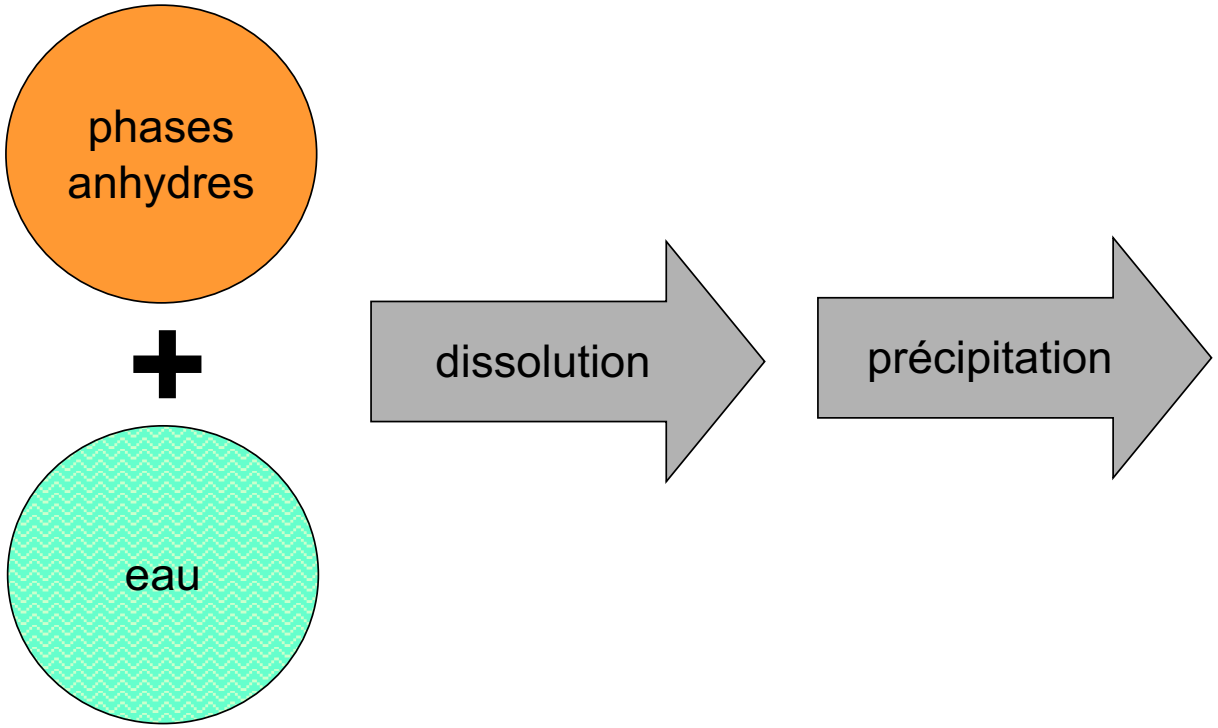
Chimie d’hydratation

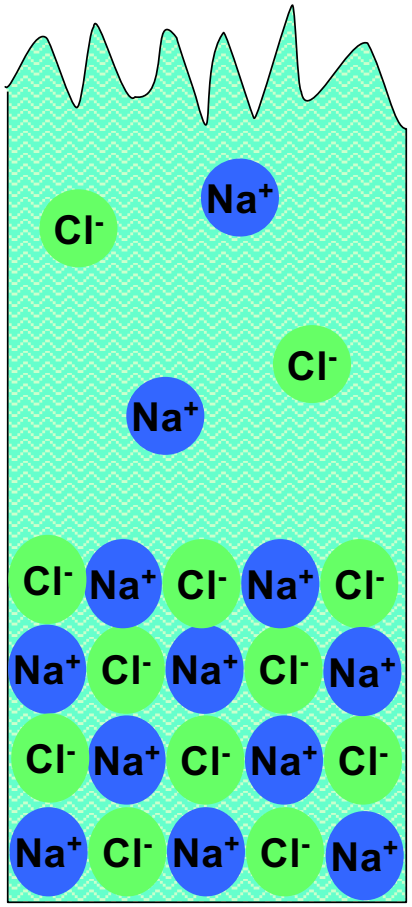
Hydratation
transformation de pâte fluide
en solide rigide



Hydratation

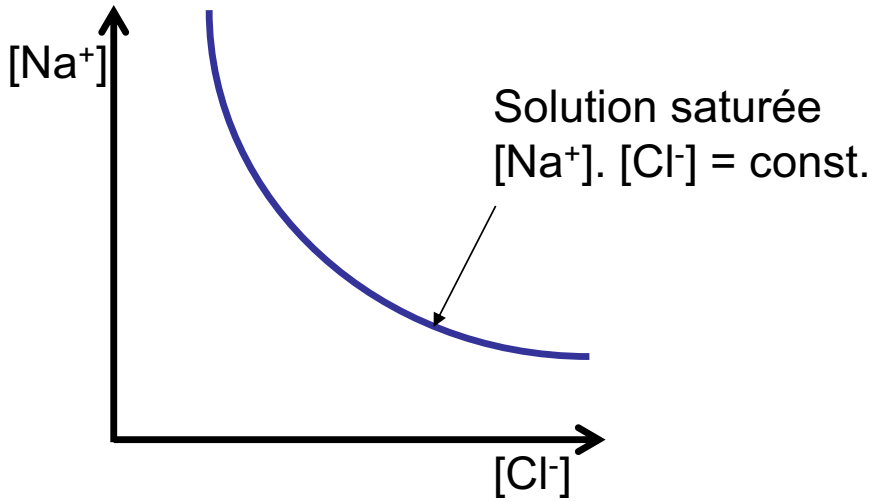


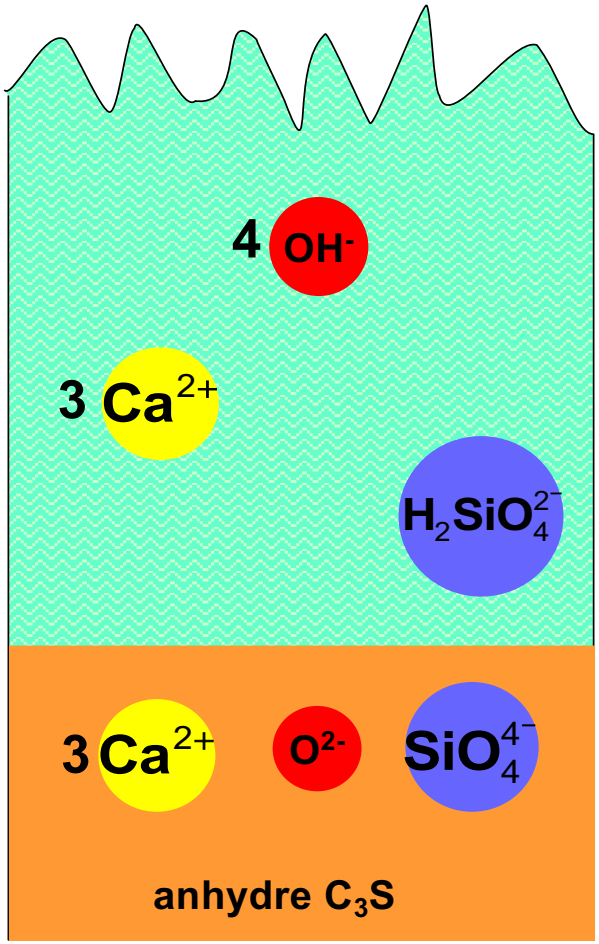
Dissolution

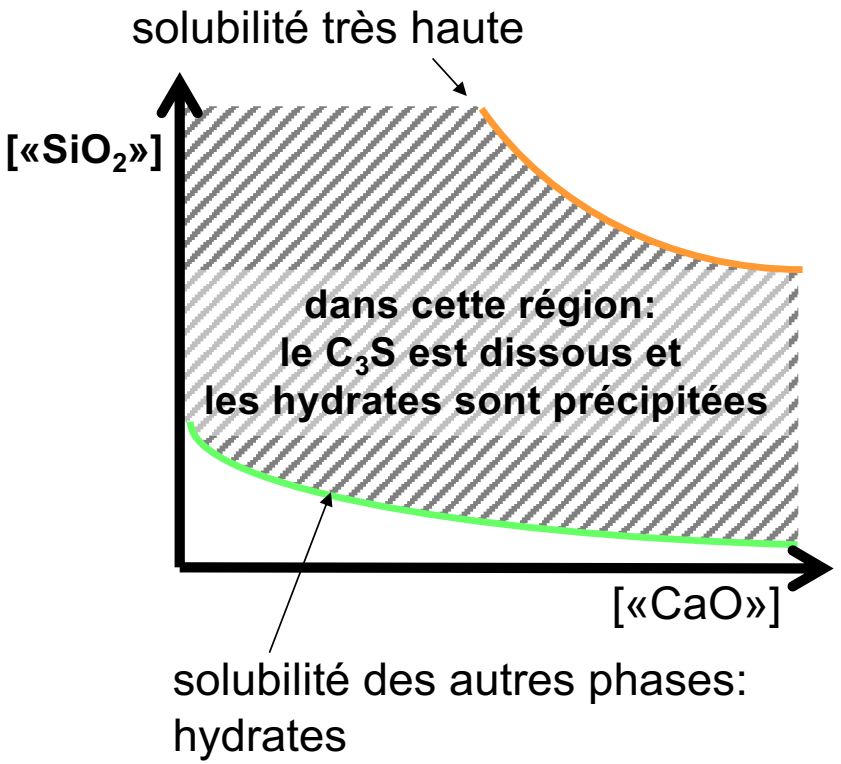


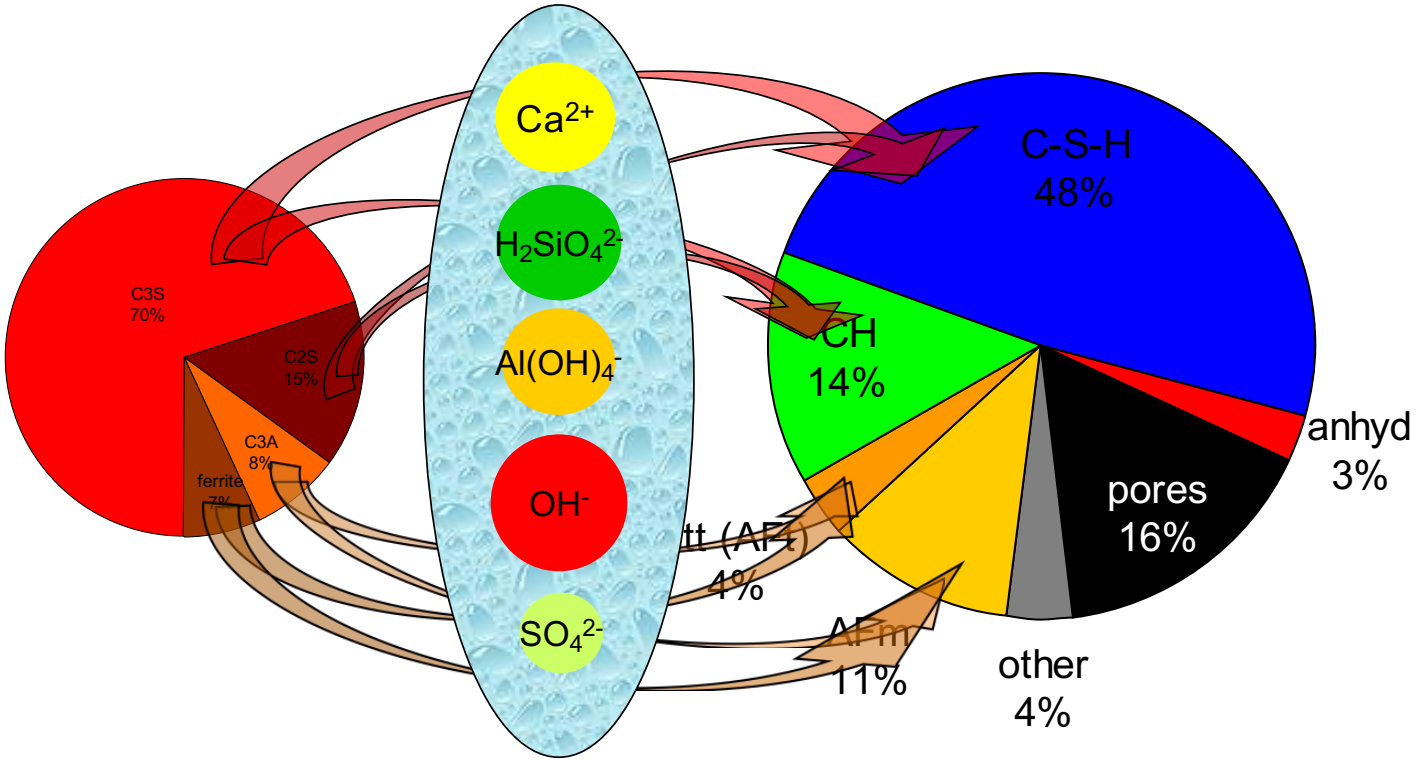
Ex. sel de table:
les ions dans un solide entré en solution.

Il y a une ***« limite de solubilité »***
au-delà de laquelle la solution est
« saturée »

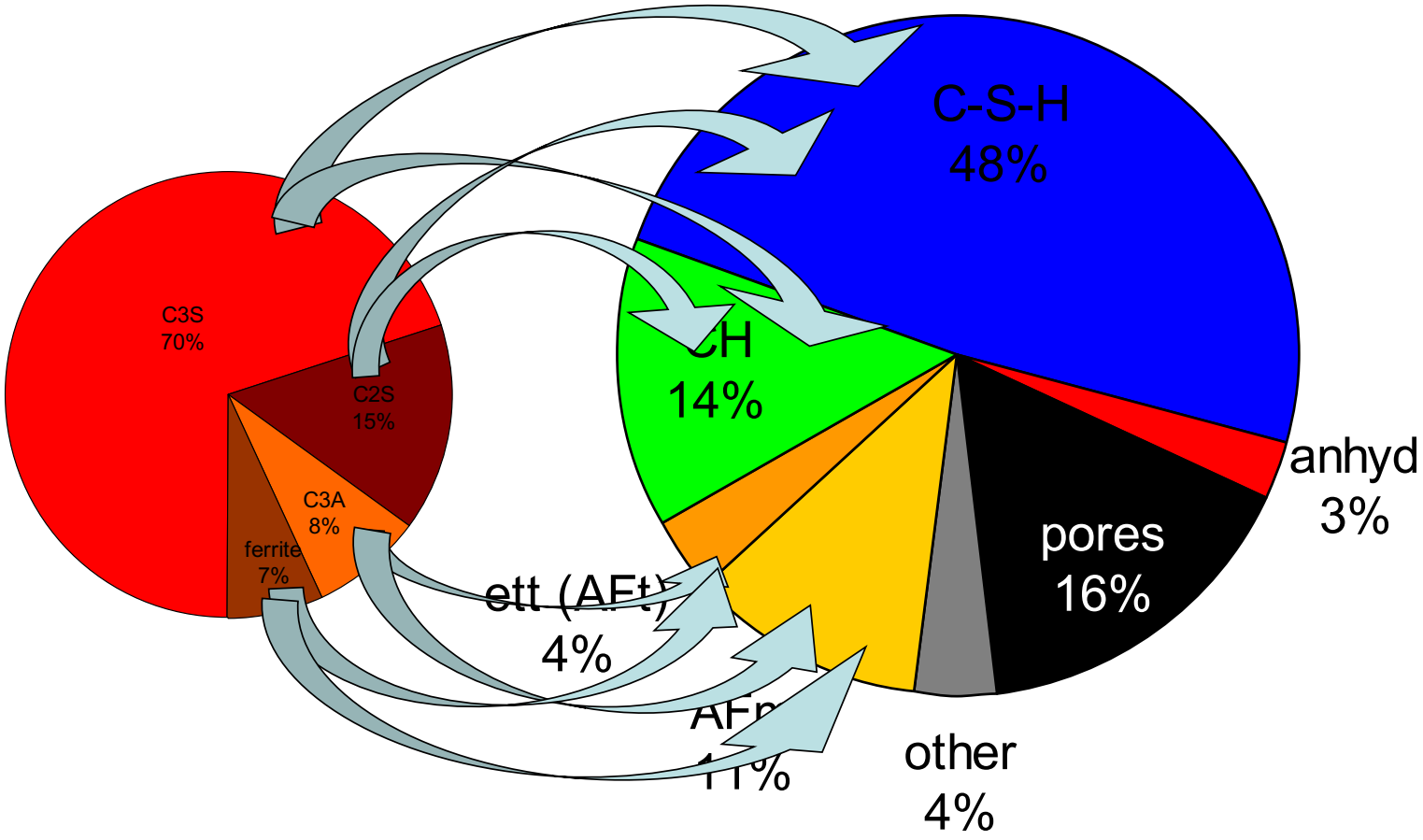



4 OH-
3 Ca2+
H2SiO42−
3 Ca2+
O2-
SiO44−
anhydre C3S


solubilité très haute
[«SiO2»]
dans cette région:
le C3S est dissous et
les hydrates sont précipitées
[«CaO»]
solubilité des autres phases:
hydrates


C3S
70%
C2S
15%
C3A
8%
ferrite
7%
Ca^{2+}
$H_2SiO_4^{2-}$
$Al(OH)_4^-$
OH^-
SO_4^{2-}
C-S-H
48%
CH
14%
anhyd
3%
pores
16%
tt (AFt)
4%
AFm
11%
other
4%

Phases present – 14 month paste from Taylor

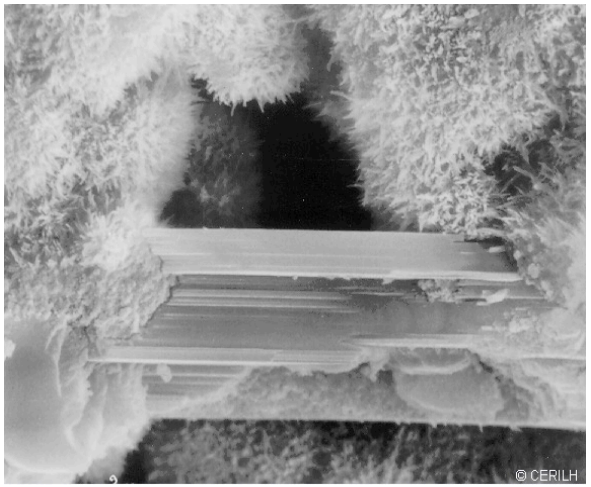


Hydration of calcium silicates : C_3S and C_2S

calcium hydroxyde
Hydrated lime
portlandite
$Ca(OH)_2$
CH

crystalline
hexagonal morphology

~ 25-28% of hydrated paste



hydrated calcium silicate
C-S-H

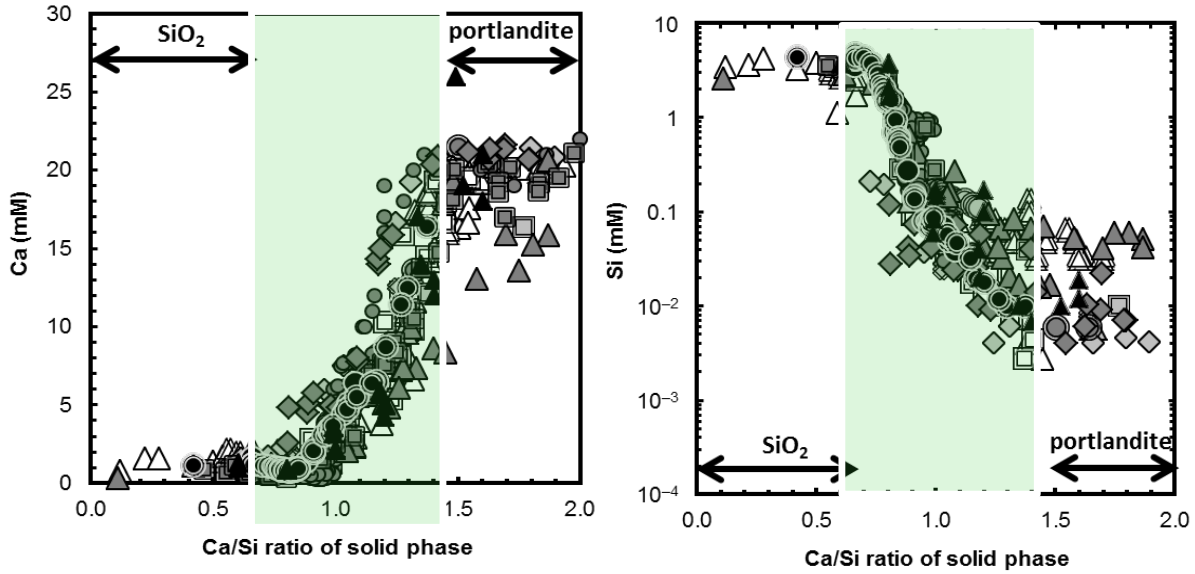
Mainly amorphous
multiple morphologies

~ 60-65% of hydrated paste

C-S-H

Definite phase, reproducible behaviour

Variable calcium to silicate ratio, depending on composition of solution

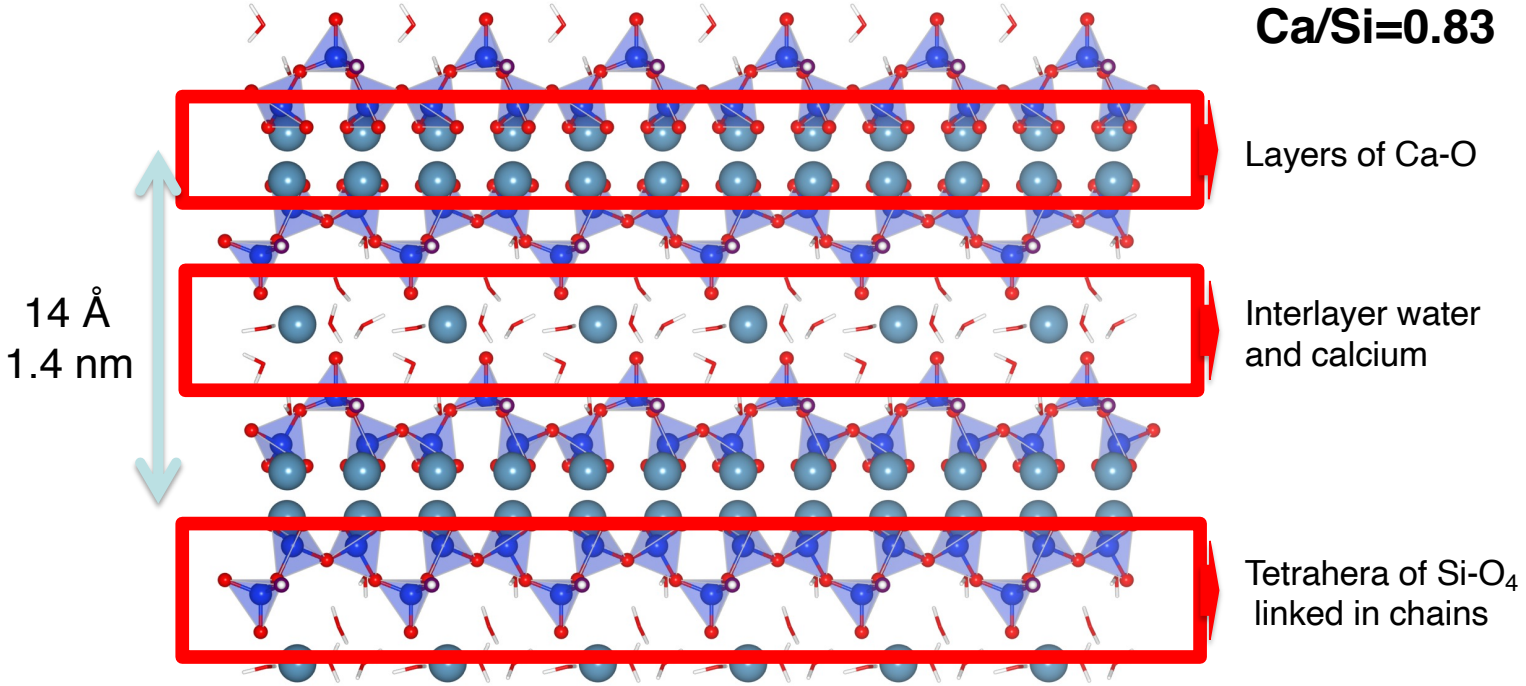


Ca/Si =
0.7 to 1.5
for “synthetic” C-S-H

1.7-2 PC pastes

Lothenbach, Nonat (2015) CCR

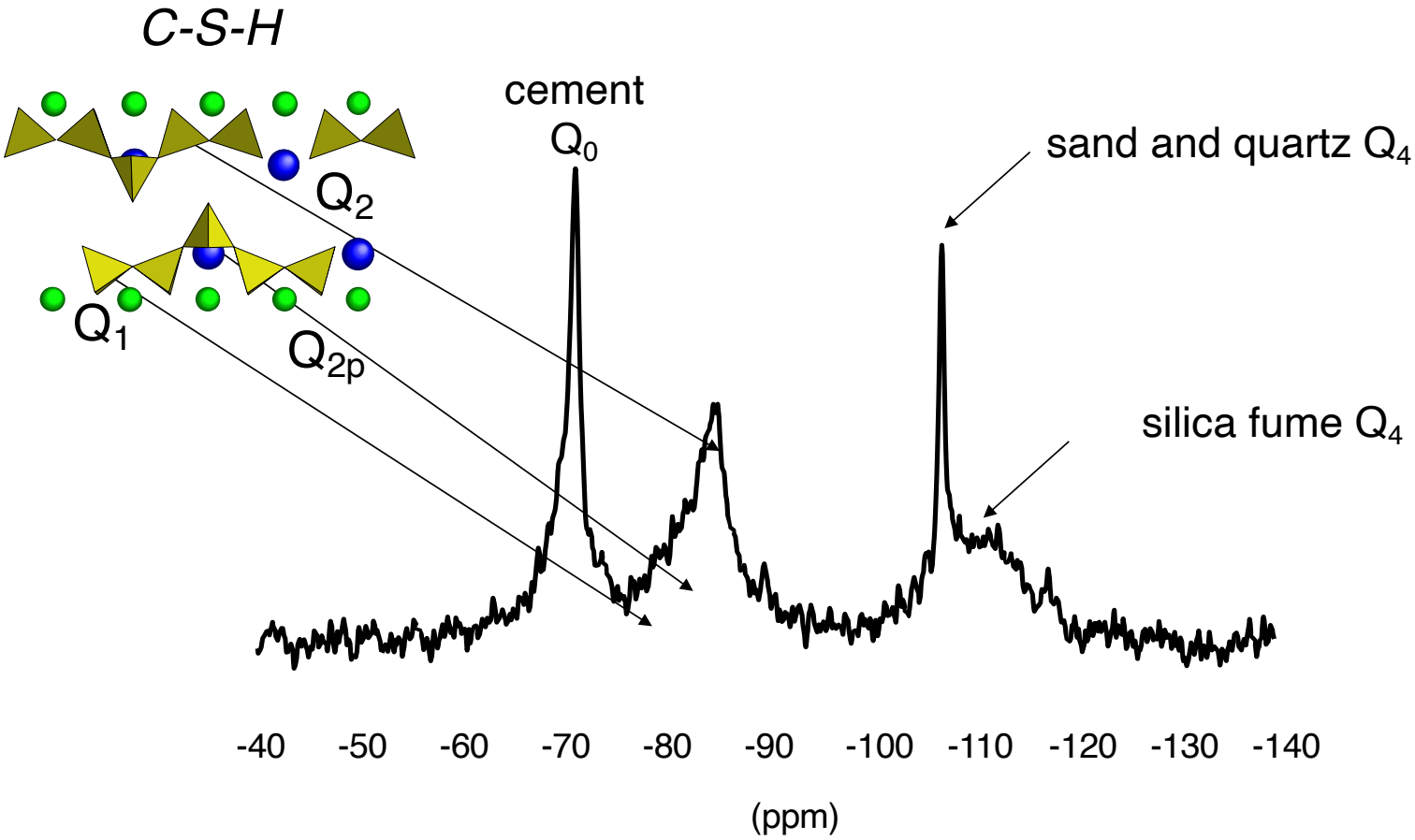
Structure based on natural mineral tobermorite



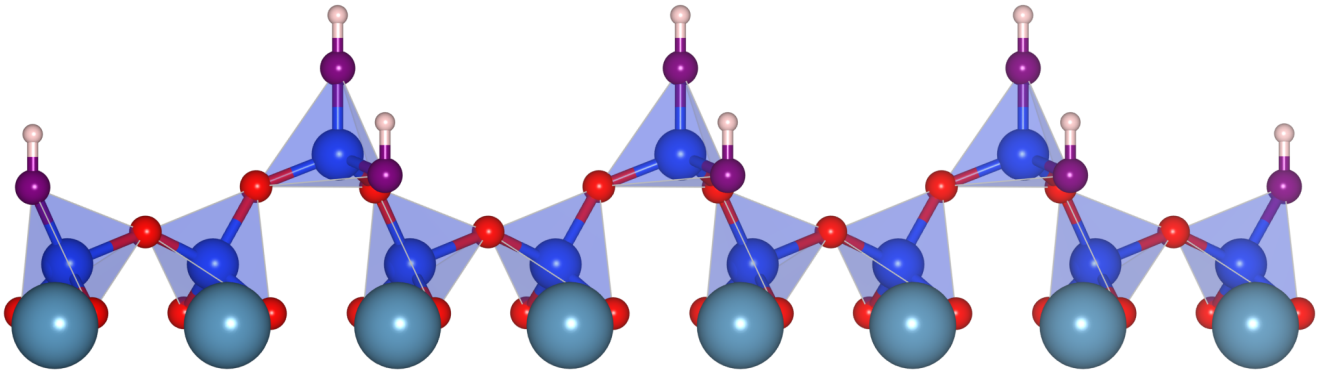
Images by Aslam Kunhi Mohamed

Tremendous progress in understanding C-S-H in last 20 years due to use of NMR

Silicate structures : Q groups and NMR



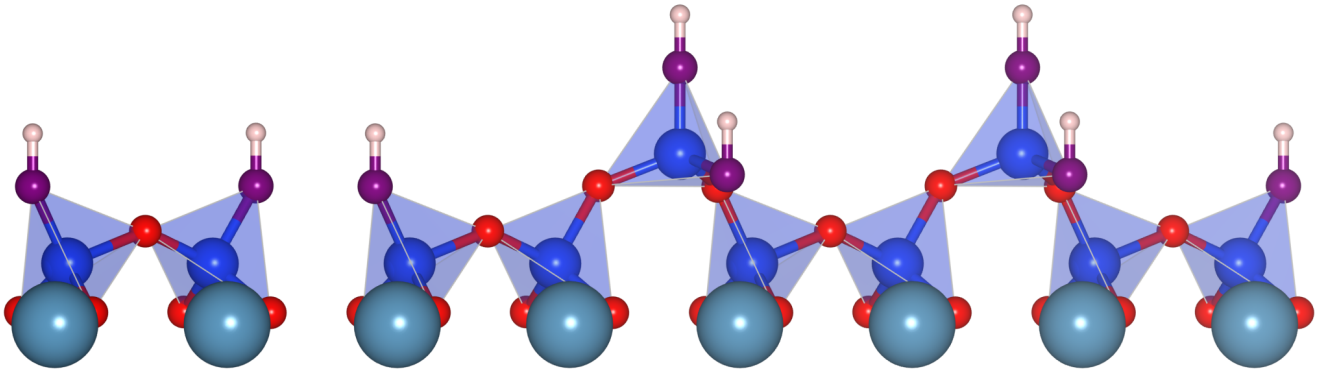
Ways to vary C/S



Ca/Si=
0.727

Full chains, terminating hydroxides

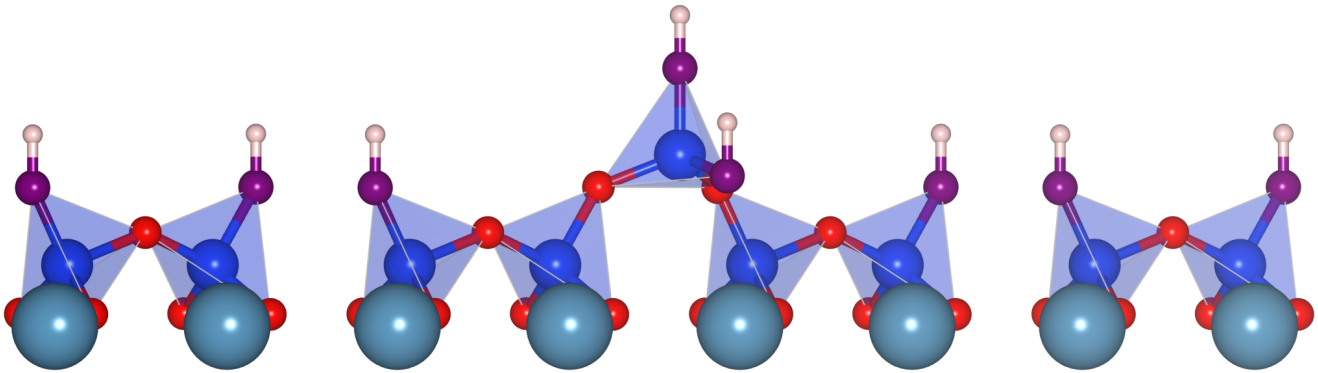
Ways to vary C/S



Ca/Si= 0.8

Missing bridging tetrahedra

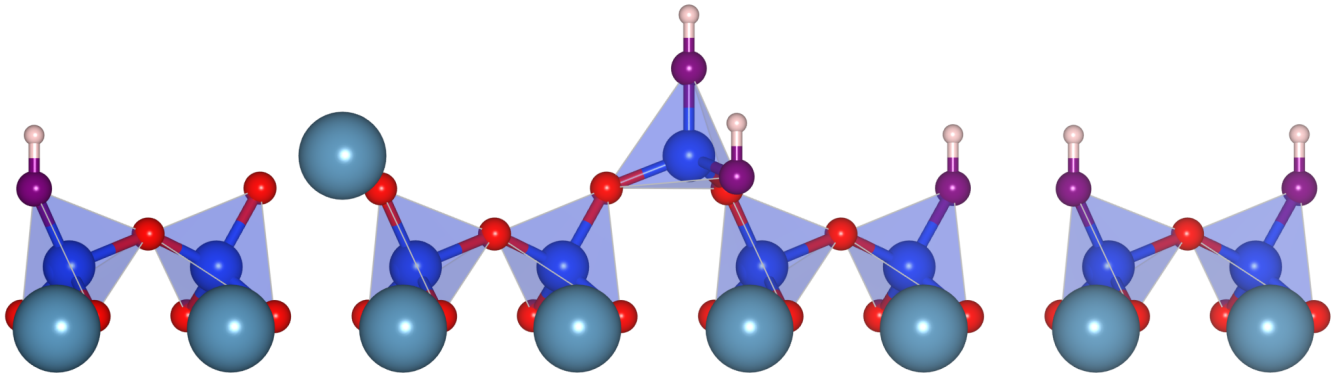
Ways to vary C/S



Ca/Si=
0.9

Missing bridging tetrahedra

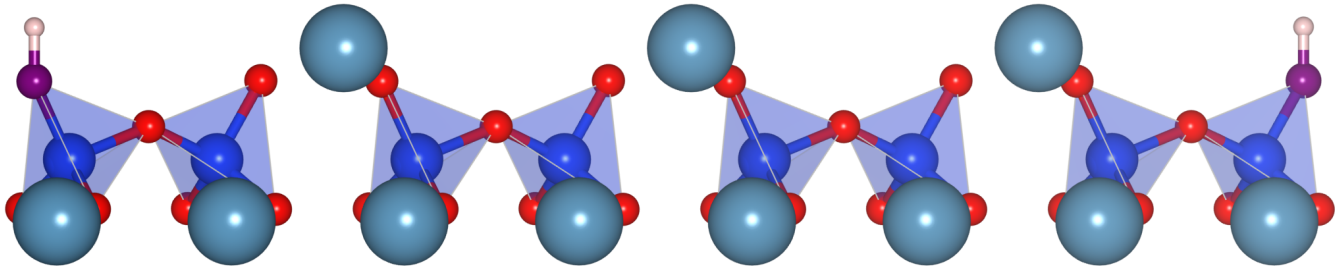
Ways to vary C/S



Ca/Si=
1.0

Calcium replacing two terminating hydroxides

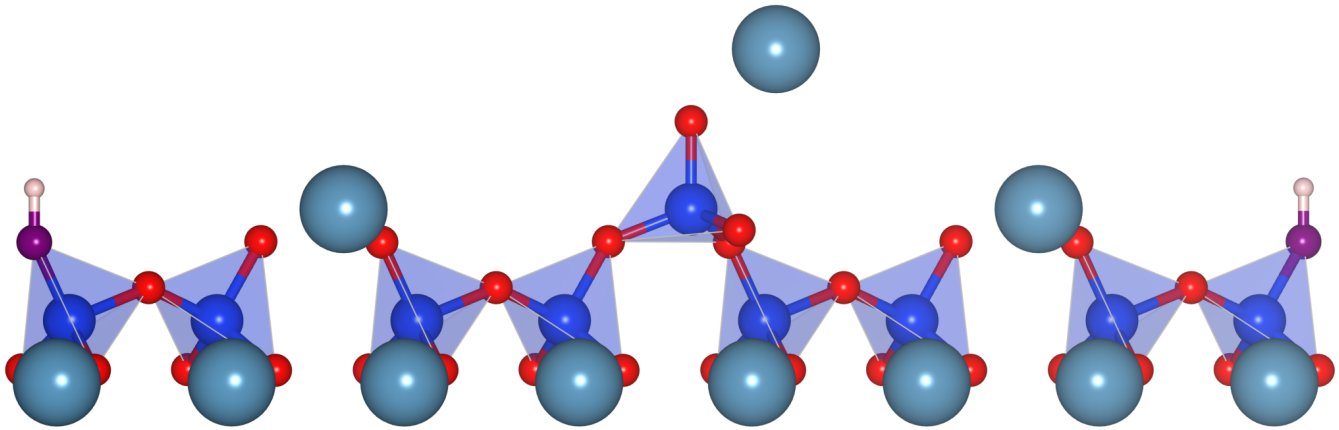
Ways to vary C/S



Ca/Si=
1.38

Calcium replacing two terminating hydroxides

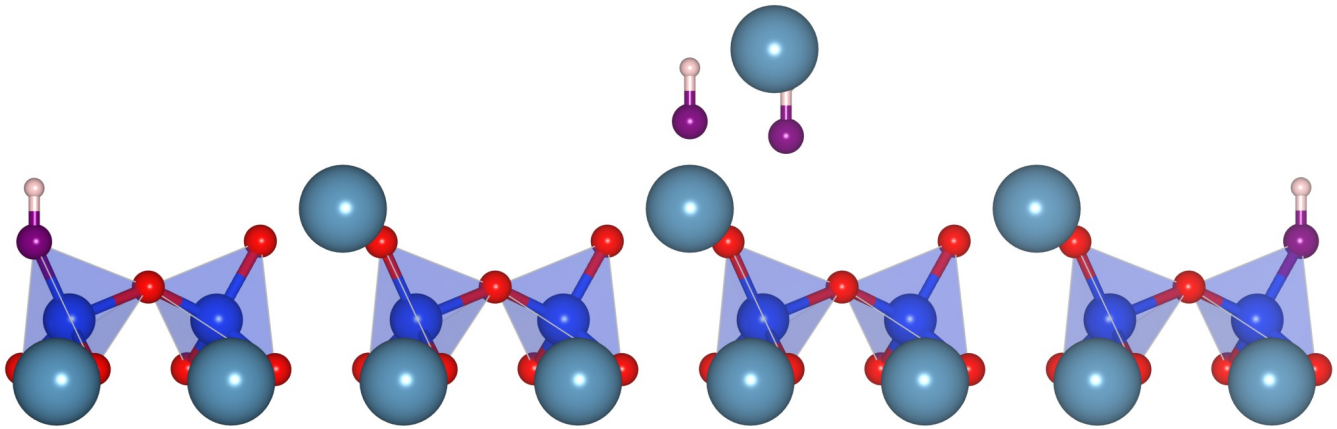
Ways to vary C/S



Ca/Si=
1.22

Calcium in interlayer

Ways to vary C/S



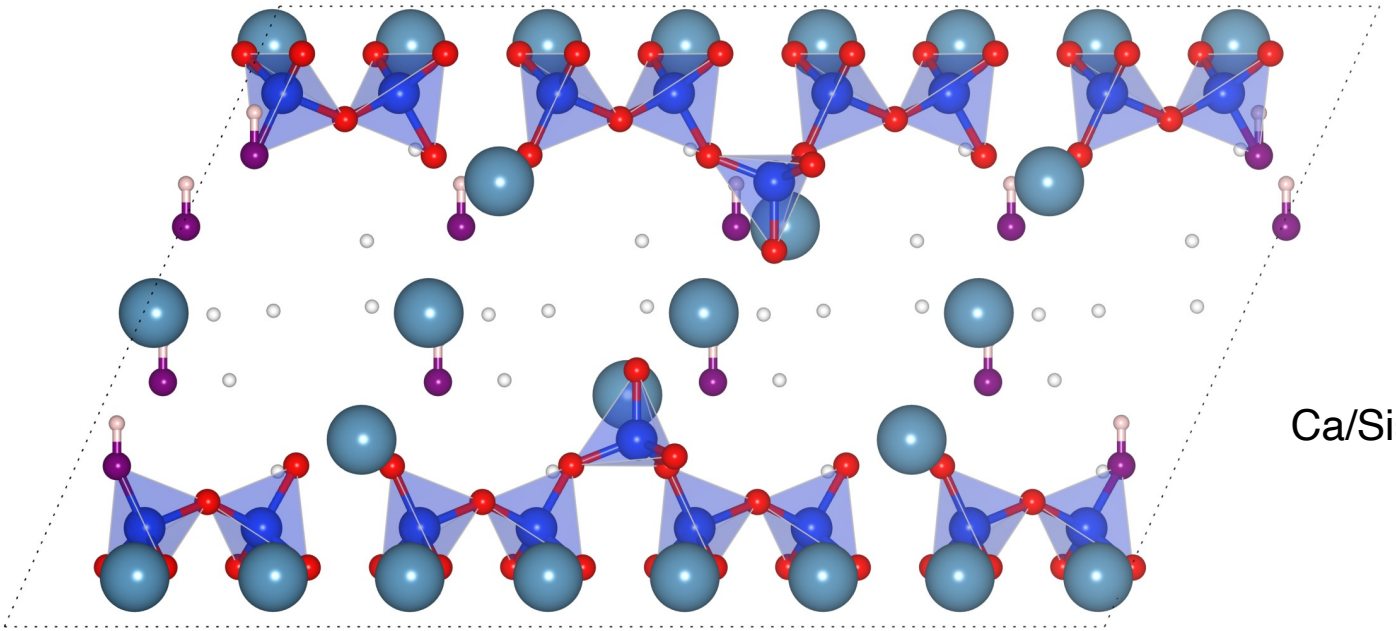
Ca/Si= 1.5

Calcium in interlayer

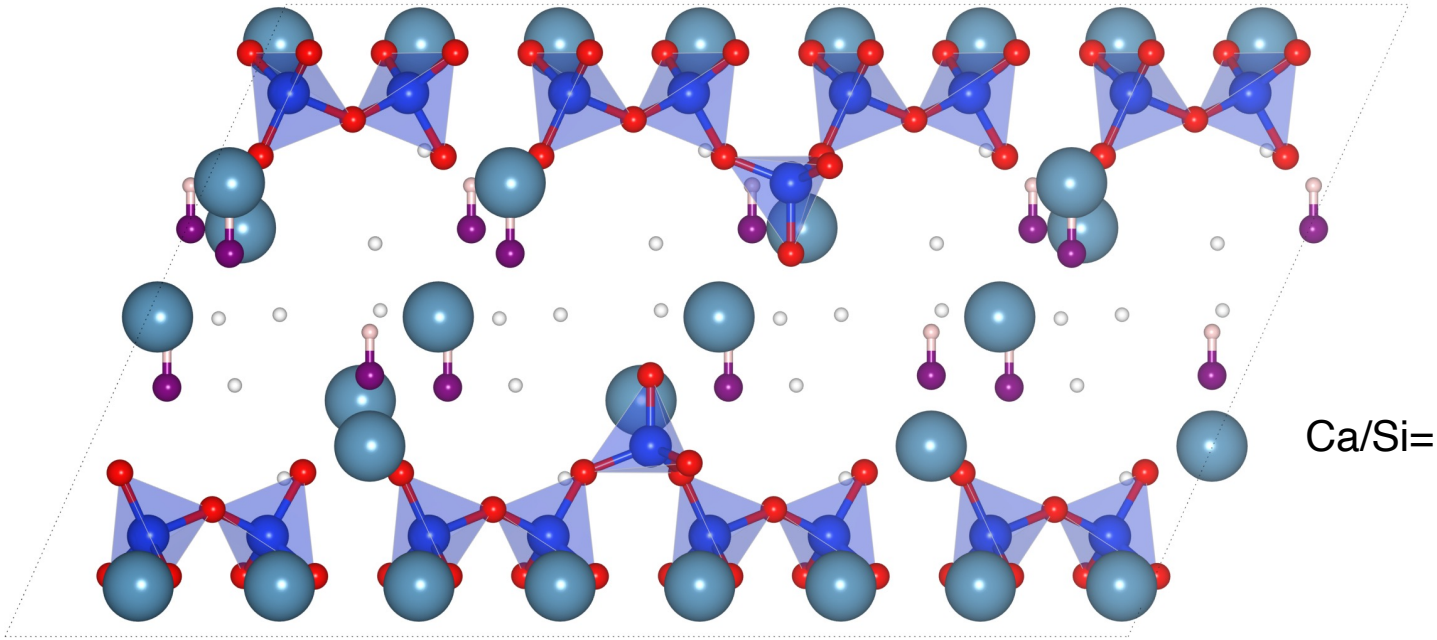
3 mechanisms

- Missing bridging tetrahedral
- Calcium replacing terminating hydrogens
- Calcium in interlayer

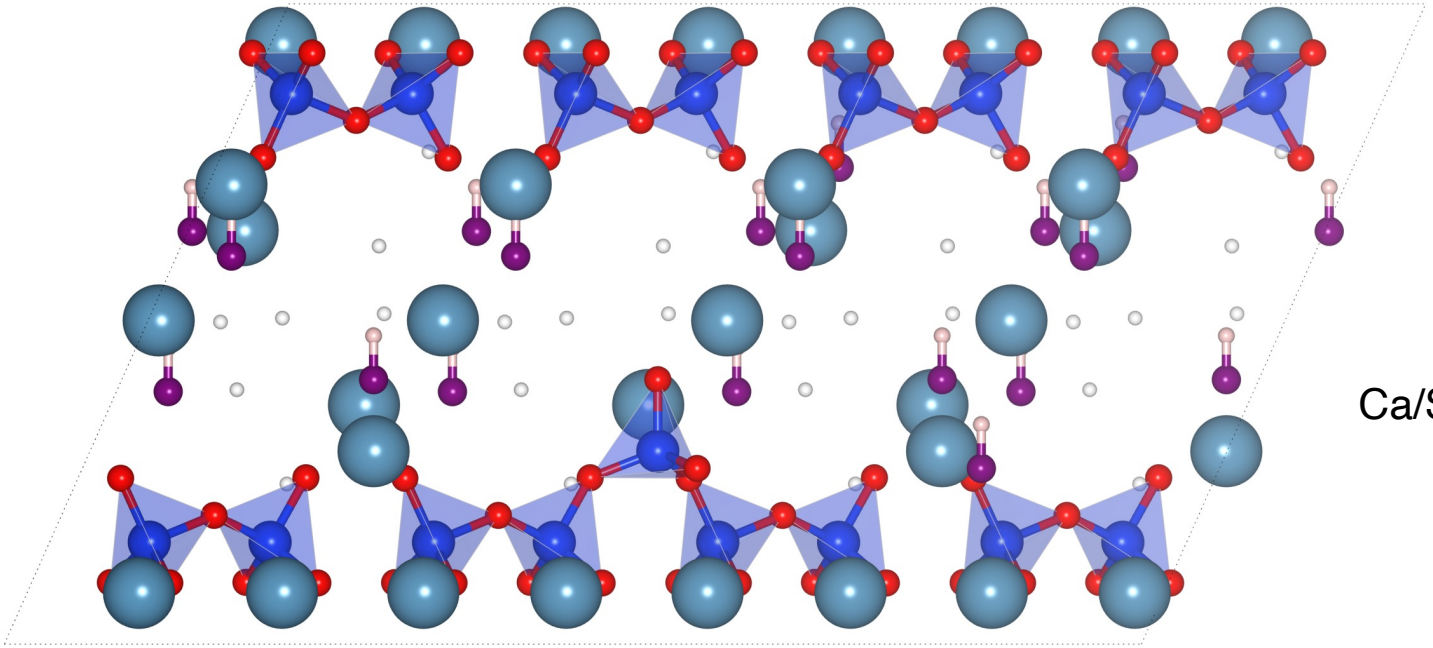
- No unique way to get a given C/S
- Structure probably has random organisation of these defects:
  - One reason for low crystallinity by X-rays



Ca/Si= 1.44

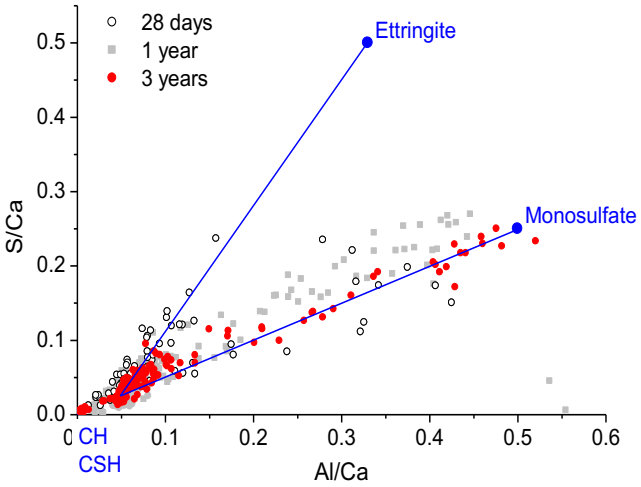


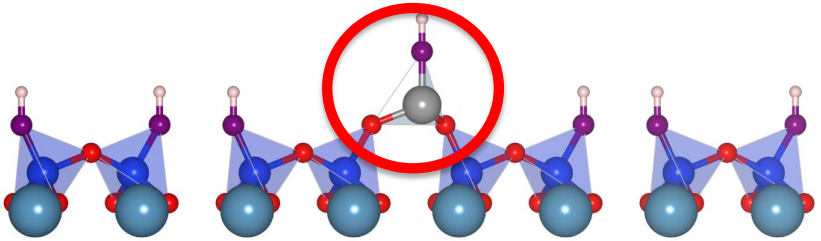
Ca/Si= 1.72



Ca/Si= 1.94

C-S-H: Si substitution by Al





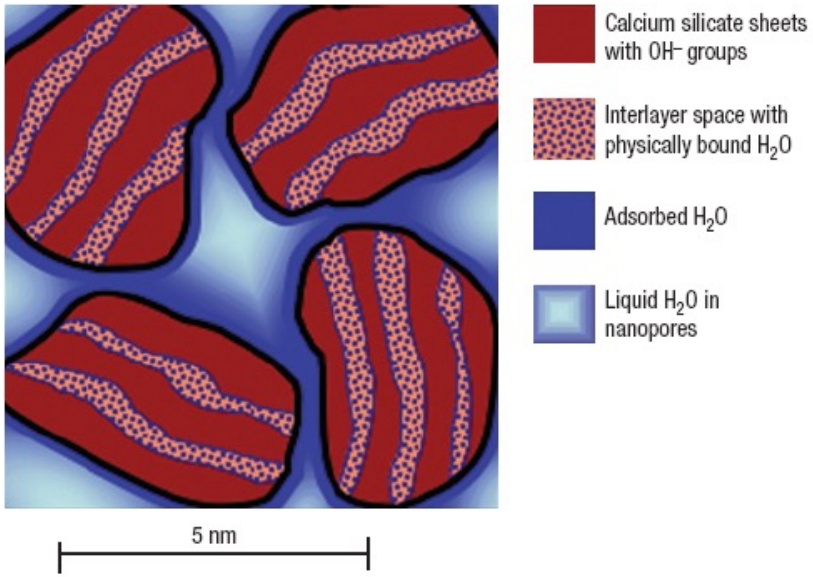
OPC pastes: Al/Ca ~ 0.05 ; Al/Si ~ 0.1
Higher with Al rich SCMs

Location in bridging sites

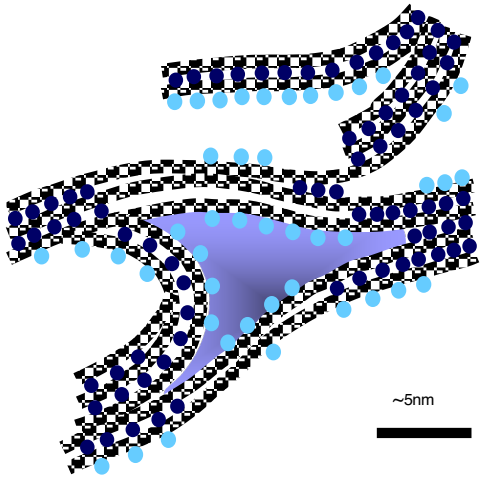
Structure at “meso” level

- No long range order
- “intrinsic” porosity of 26-28% (Powers)
  – “*gel porosity*”
  - from drying – therefore upper limit
- Scattering experiments (neutron, X-ray) and proton NMR indicate “characteristic size” of about 4-5 nm

Two schools of thought

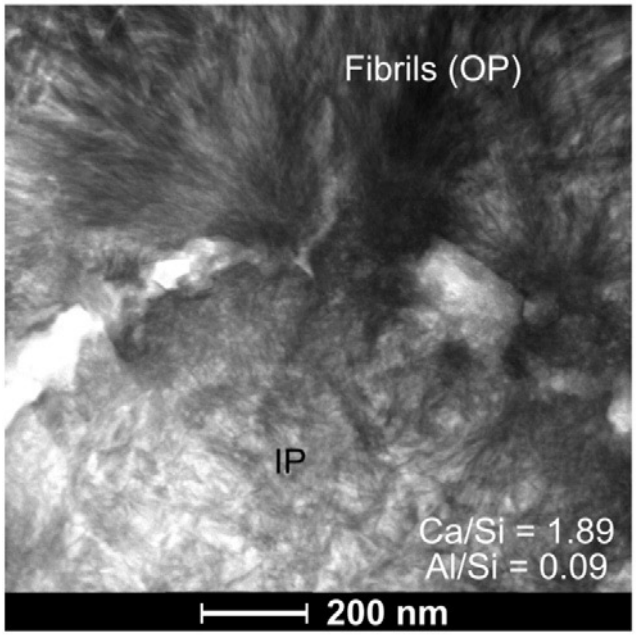


“Jennings” model
Discreet colloidal nanoparticles

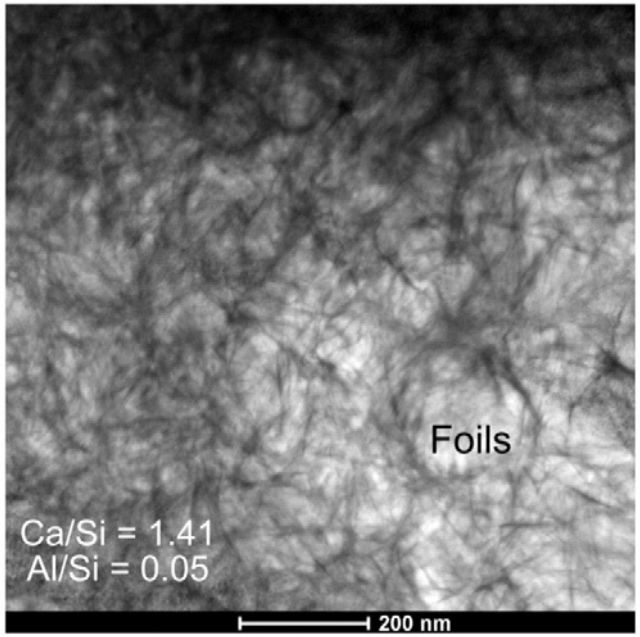


“Feldman-Serada” model
Linked nanocrystalline regions

C-S-H in cements



(a) Plain cement (PC), 90 days, 20°C

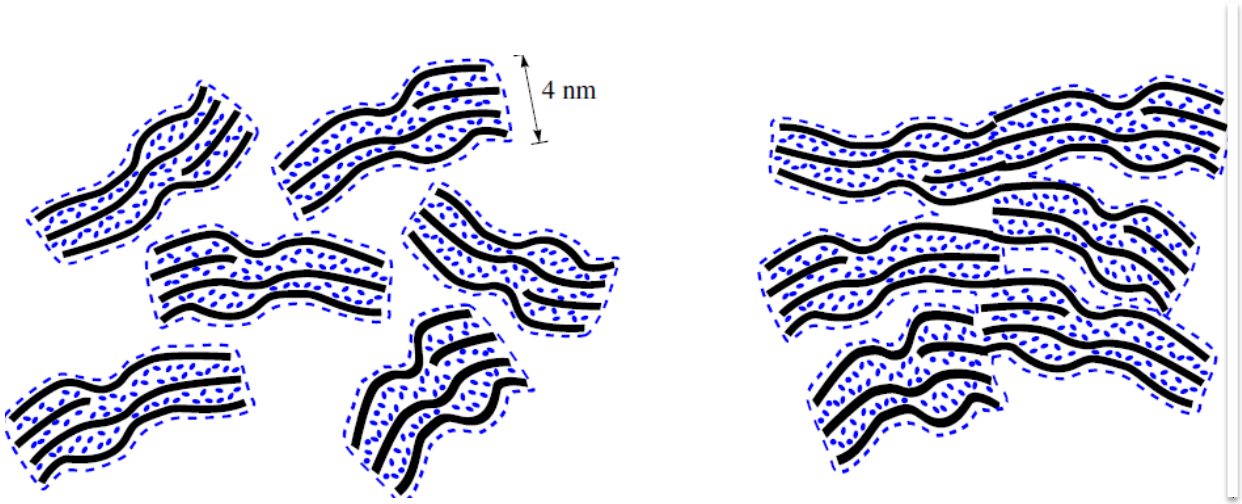


(b) PC 10SF, 90 days, 20°C

Rossen ea (2015) CCR 75

Meso structure

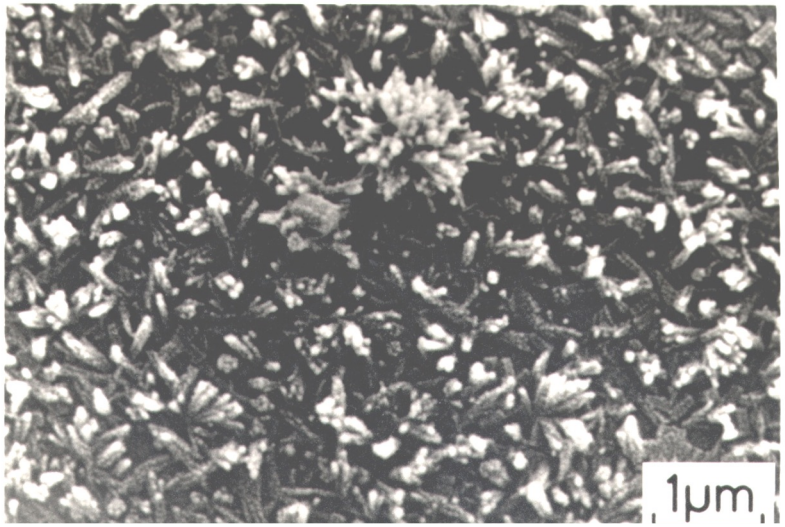
- Two interpretations of nanocrystalline nature
- The main open question is whether they are discrete or linked by sheets

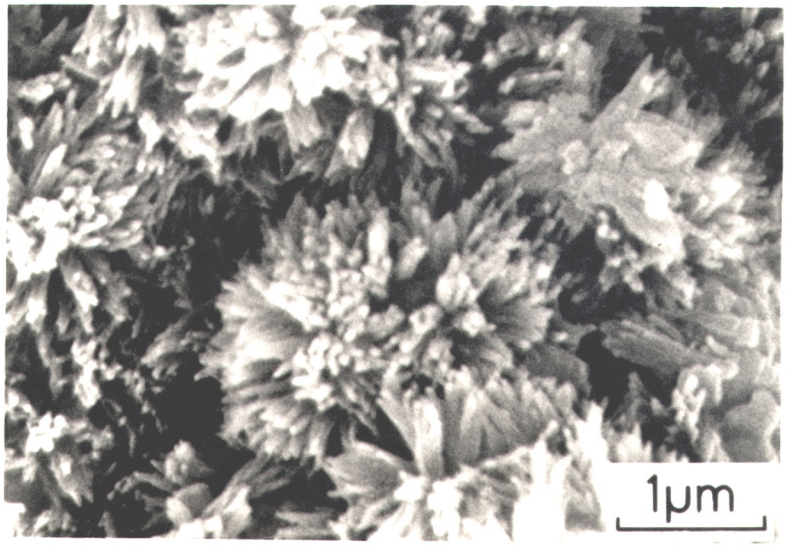


C-S-H: microstructure

SEM fracture surface

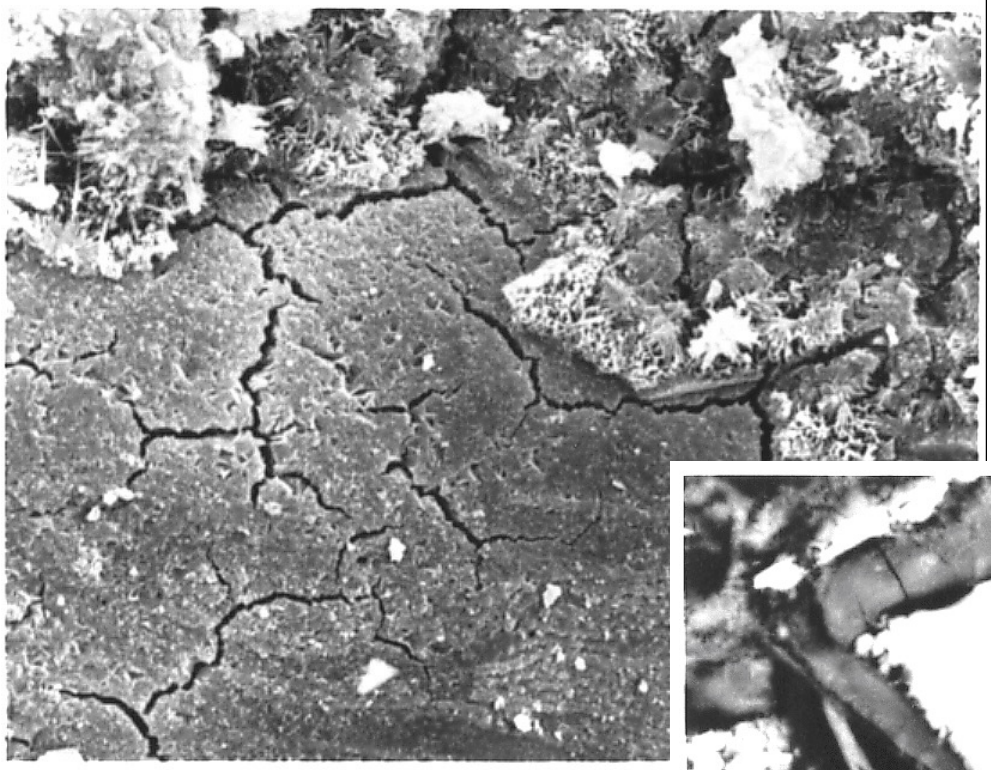
3 hrs

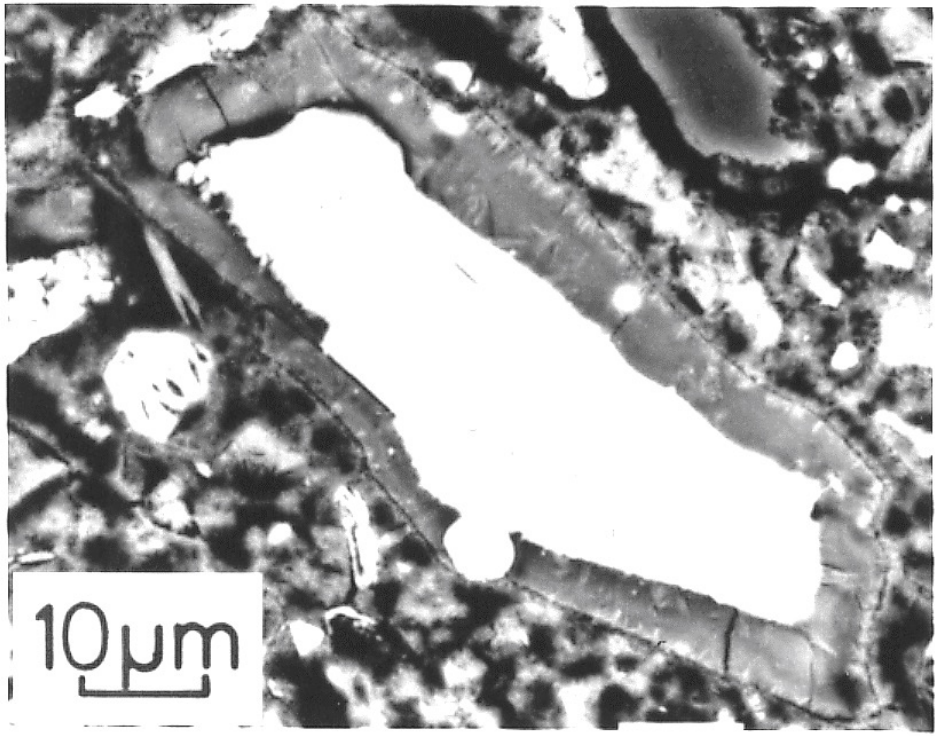




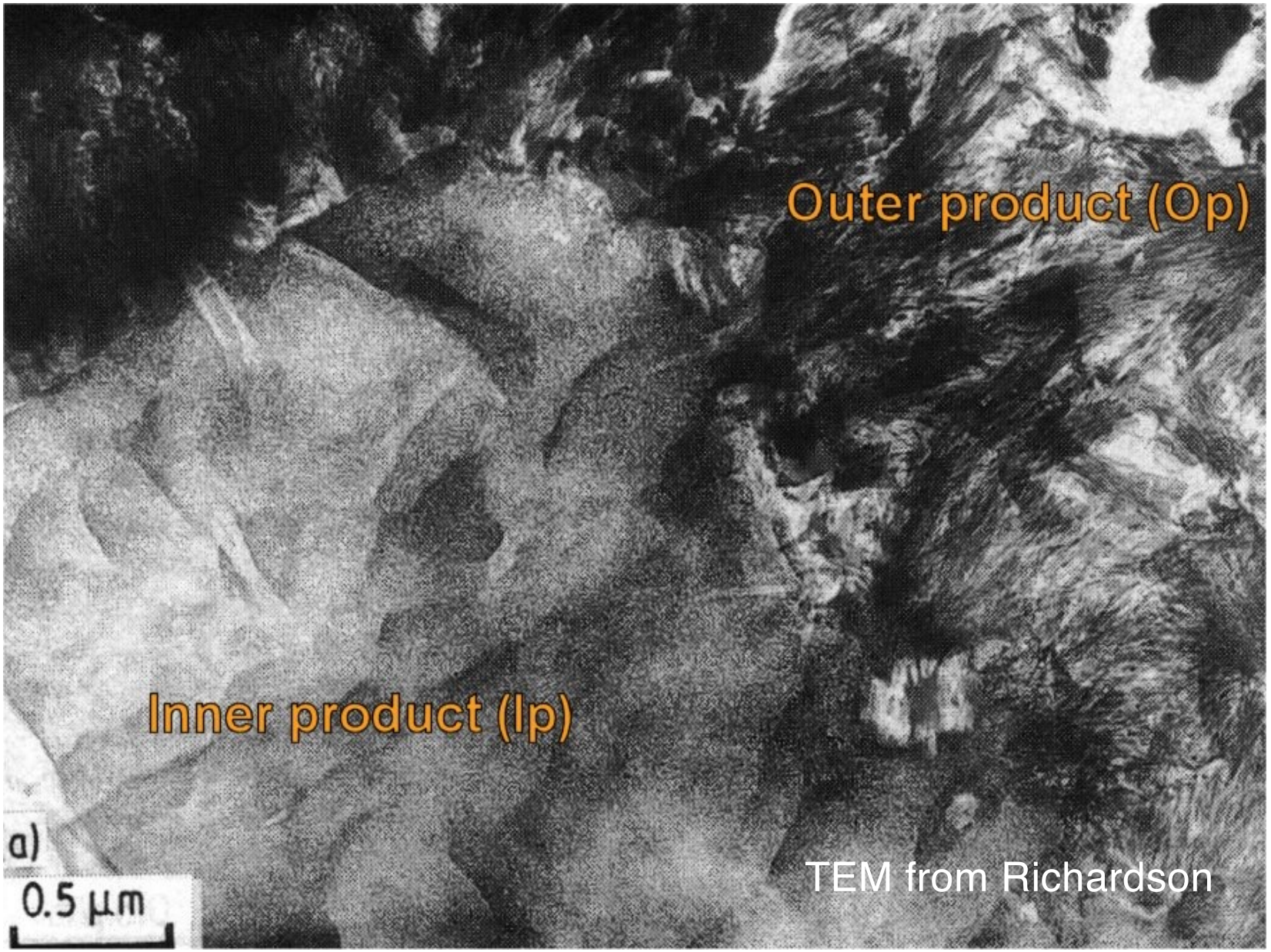
10 hrs

HVEM, wet cell, C_3S, 24hrs





Two microstructurally distinct forms:
“Outer” or “early”
“inner” or “late”


Outer product (Op)
Inner product (Ip)
a)
0.5 µm
TEM from Richardson

C-S-H summary

- Atomic level structure fairly well understood:
  - CaO sheets with chains (dimers) of SiO_4 tetrahedra attached
  - Al substitutes for Si, in bridging sites
- Meso level structure less clear
  - Nanocrystallites or nanocrystalline regions with characteristic scale of about 5nm
- Microstructure
  - Outer, formed early through solution
  - Inner formed later

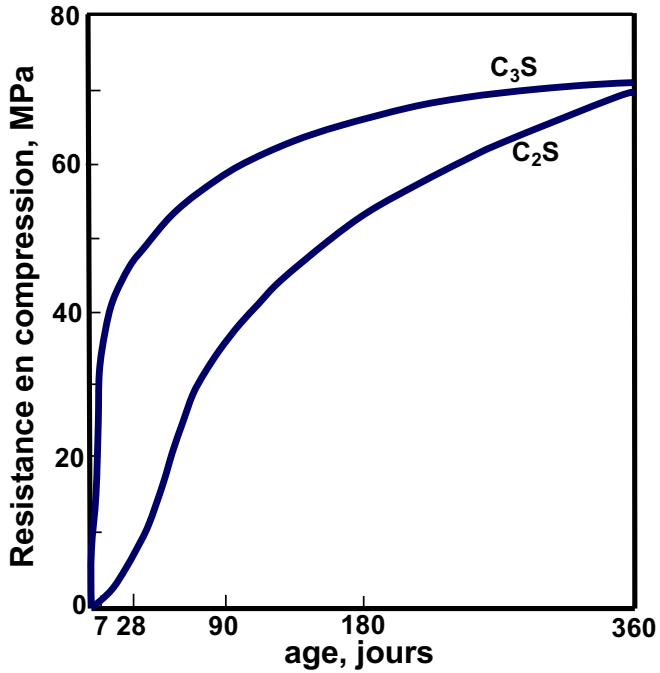
Open question

- General agreement that C-S-H consists of nanocrystalline regions:
- The main open question is whether they are discrete or linked by sheets

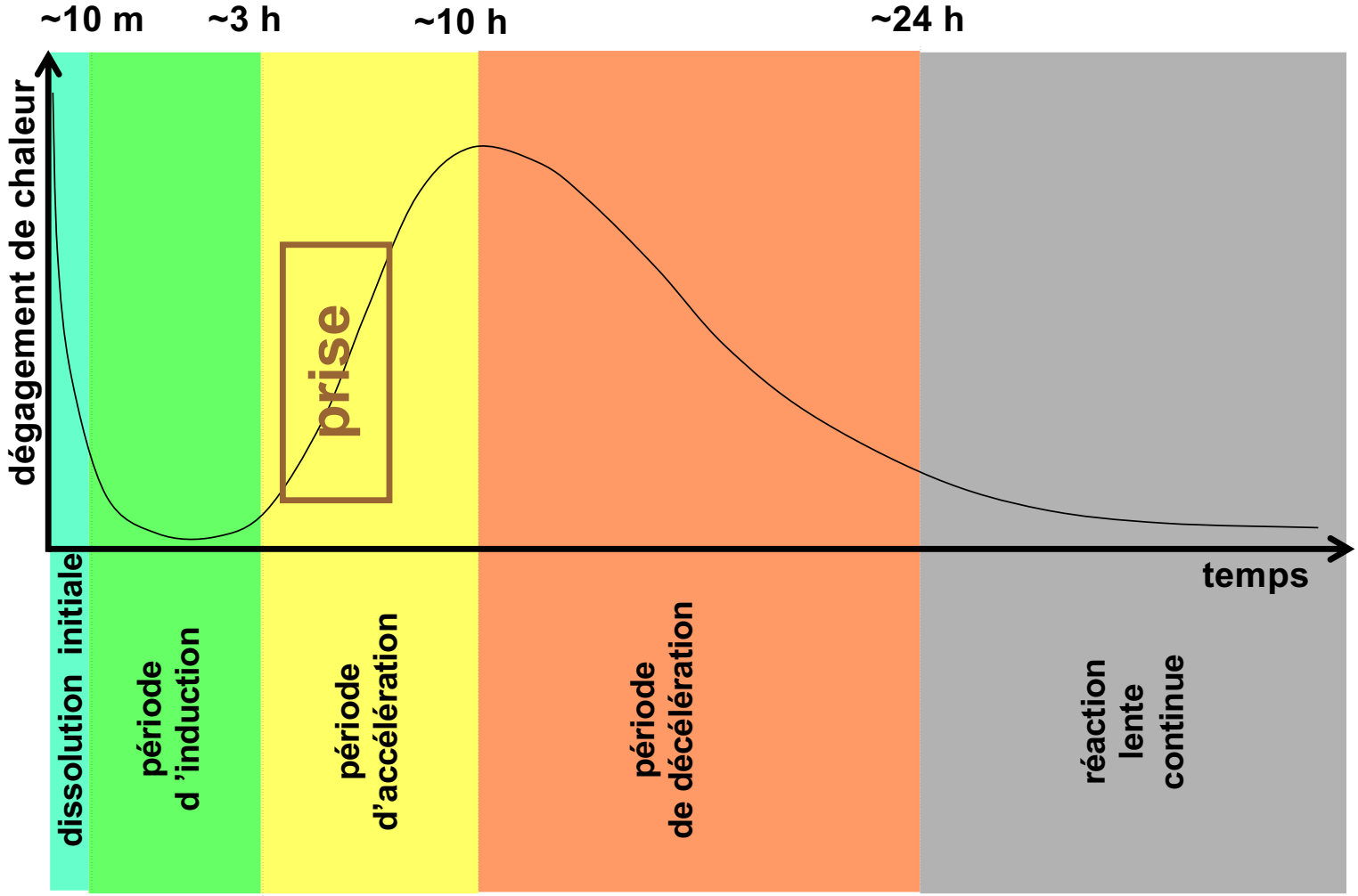
Réactions globales

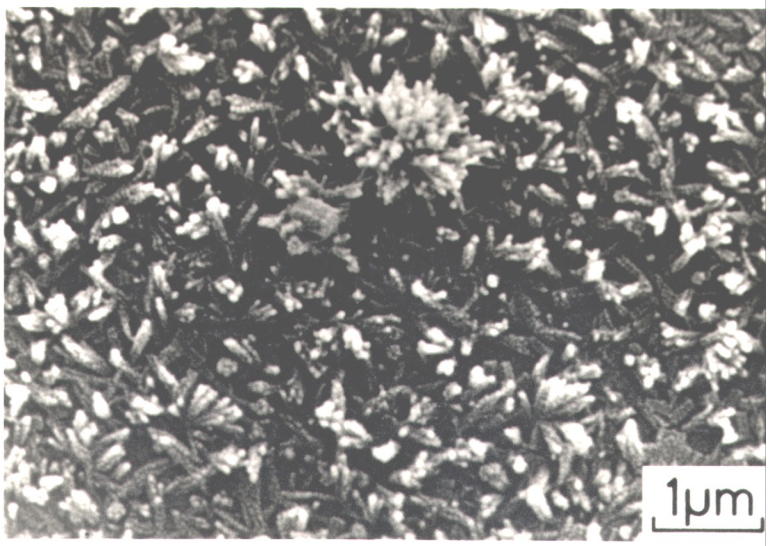
$$C_3S + 5.3H \Rightarrow C_{1.7}SH_4 + 1.3CH$$

$$C_2S + 4.3H \Rightarrow C_{1.7}SH_4 + 0.3CH$$

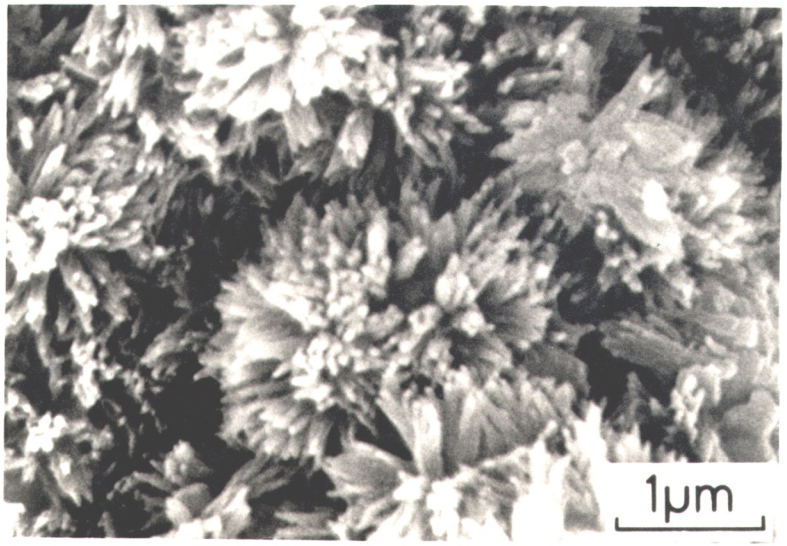


Cinétique


~10 m
~3 h
~10 h
~24 h
dégagement de chaleur
prise
temps
dissolution initiale
période d 'induction
période d'accélération
période de décélération
réaction lente continue

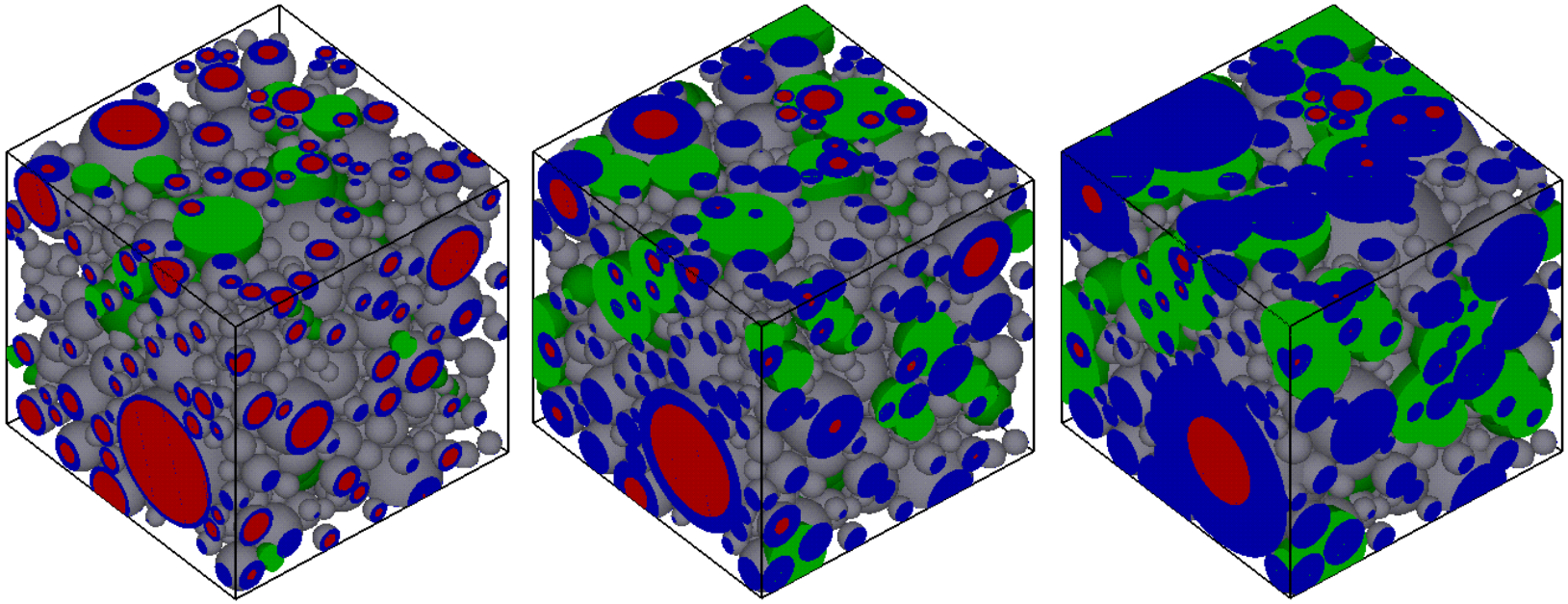


3 hrs

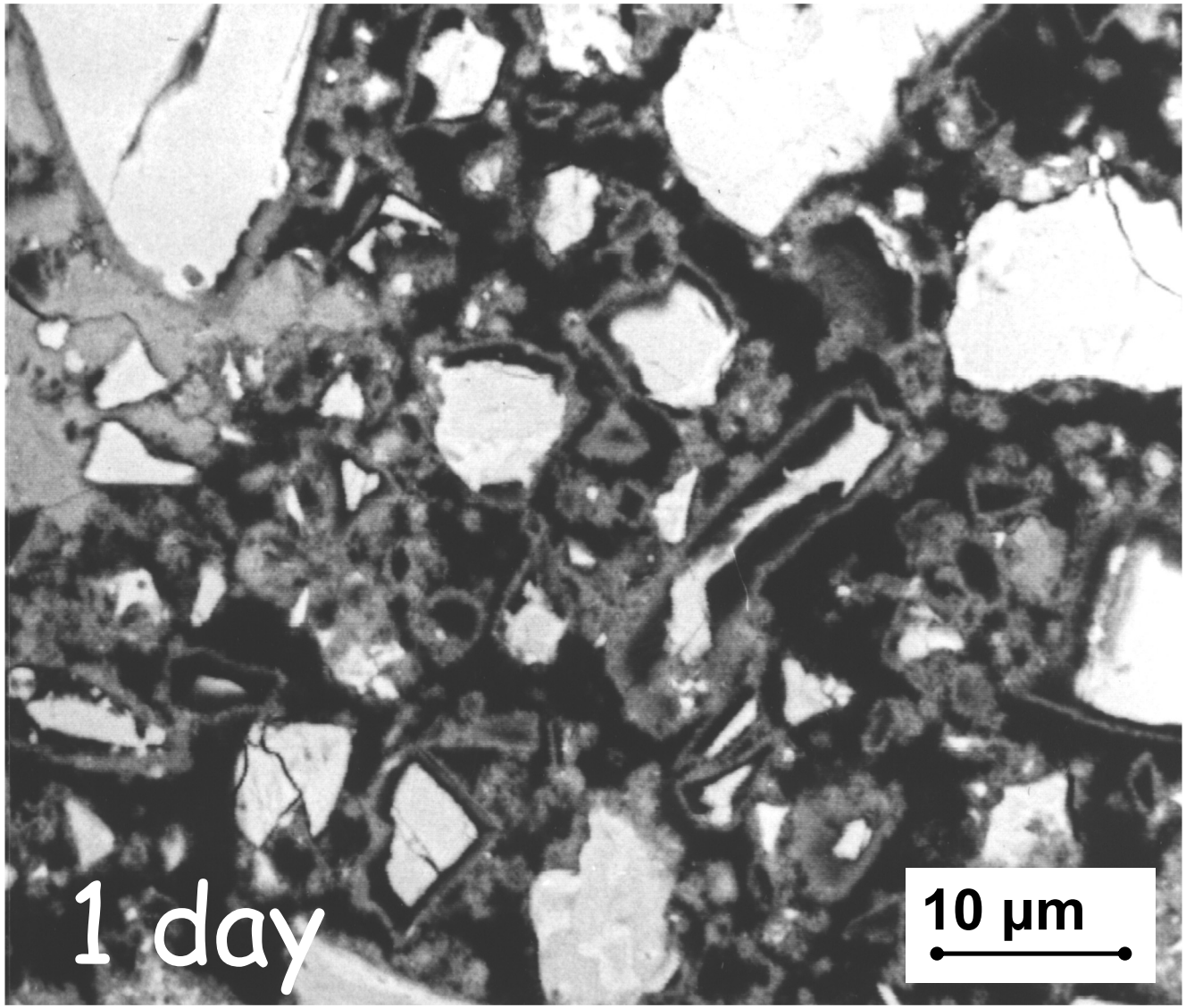


10 hrs

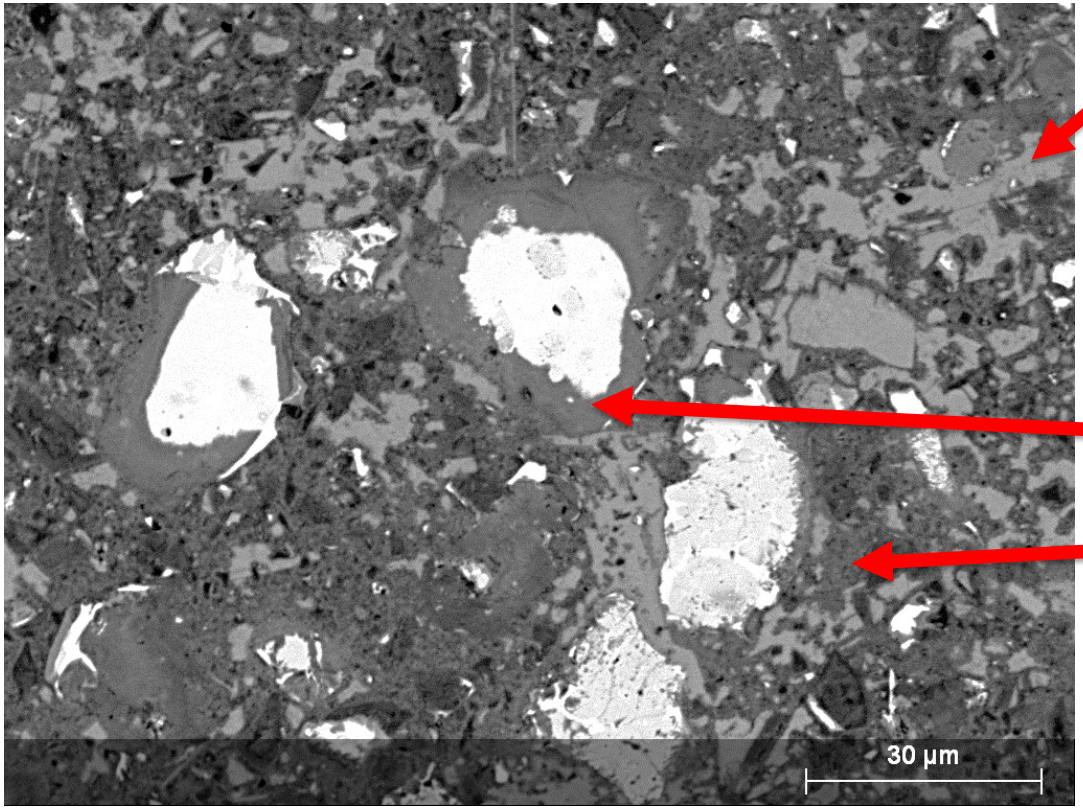
Level of connection is deceptive in 2D images



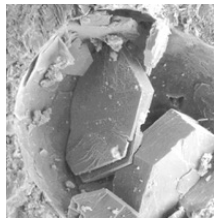
Due to close proximity of grains,
setting occurs at very low degrees of hydration ~ 2-4%


1 day
10 µm

Quelque mois

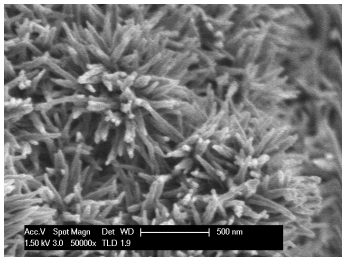


Calcium hydroxide



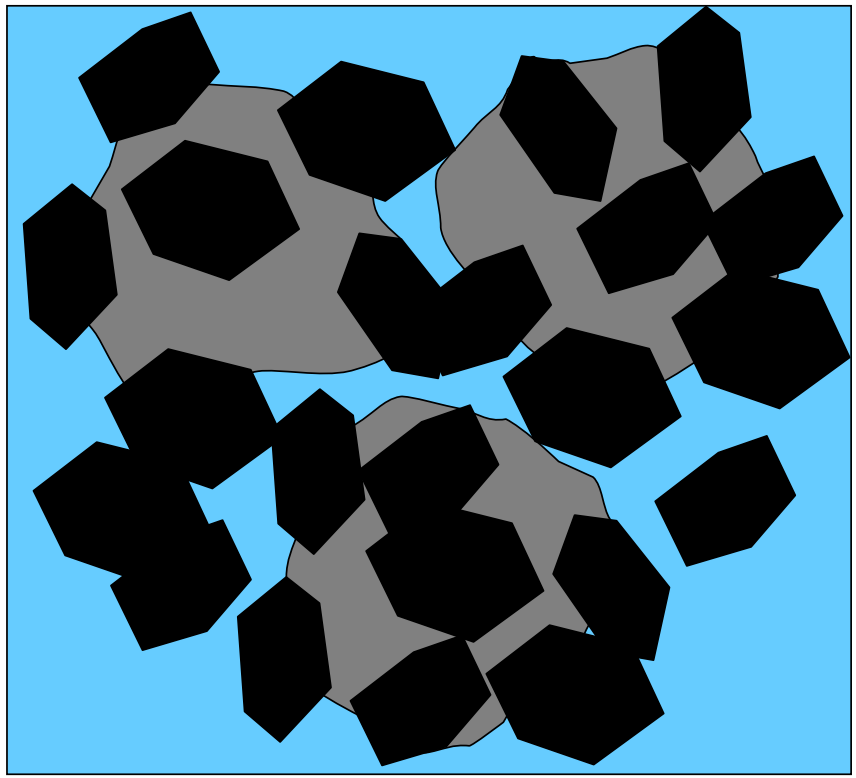
Inner C-S-H

Outer C-S-H



Coupe d'un morceau de pâte de ciment hydratée

C_3A



C_3A

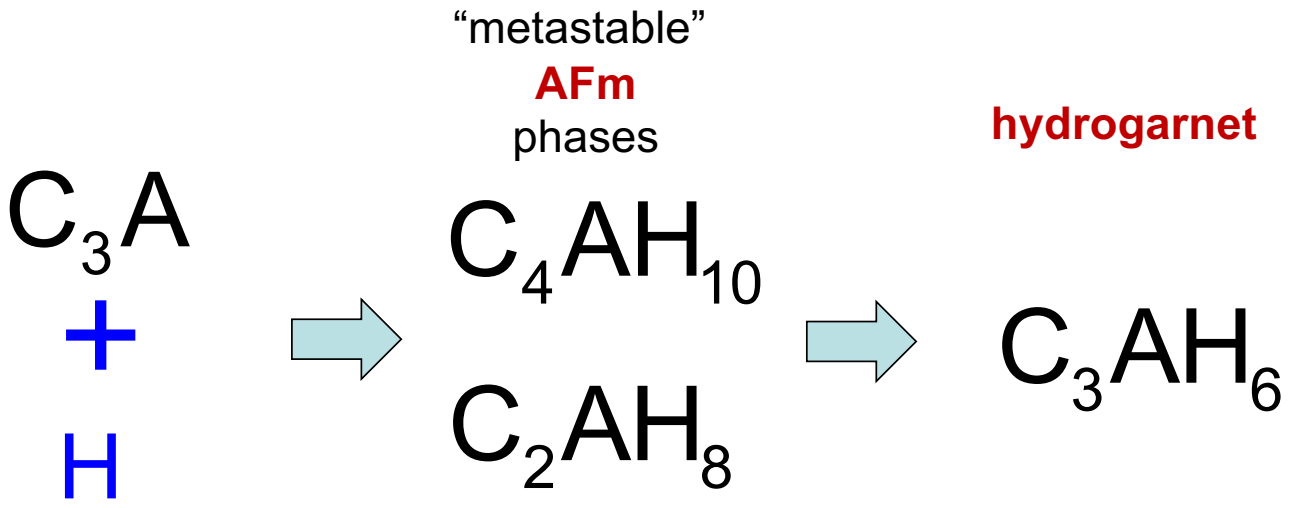
+

eau

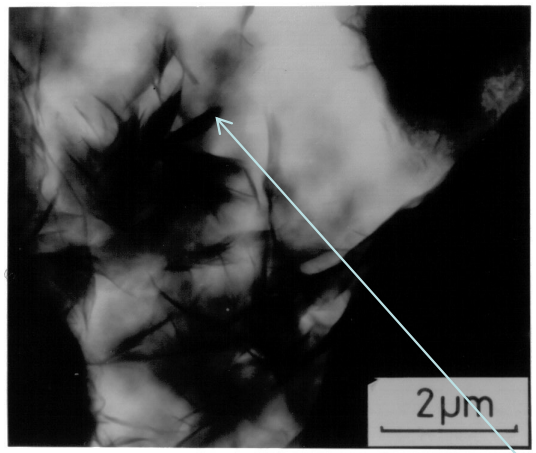
réaction rapide
grandes plaques
d'hydrates

rigidification
« prise flash »
« flash set »

Hydration C_3A without sulfate

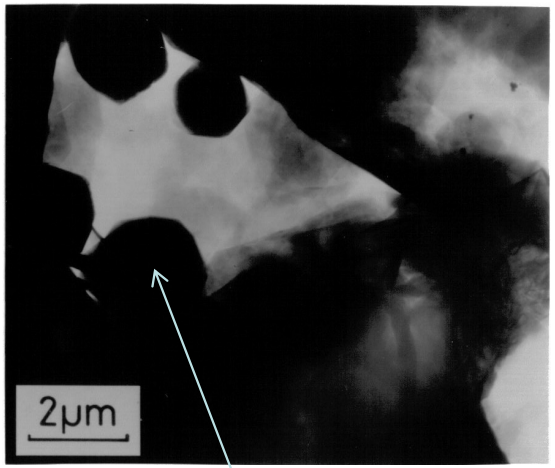


Hydration C_3A without sulfate



10 minutes

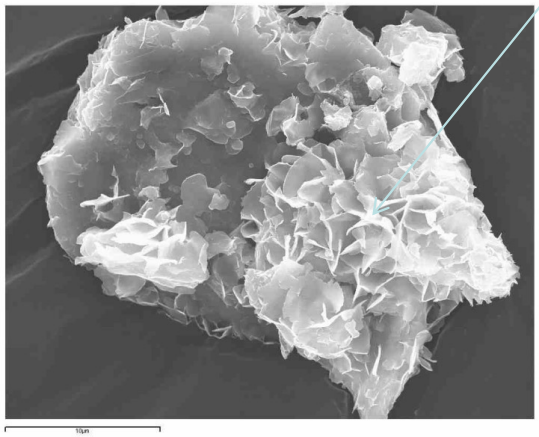
"wet" TEM
Thesis
Scrivener
1984



120 minutes

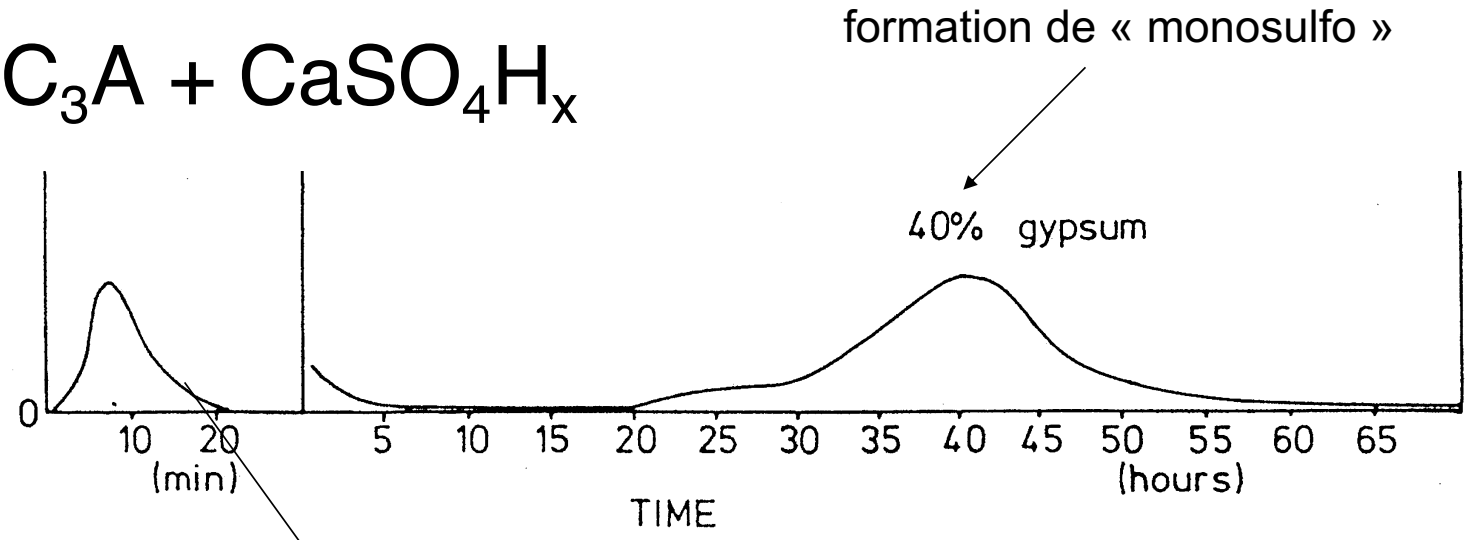
AFm

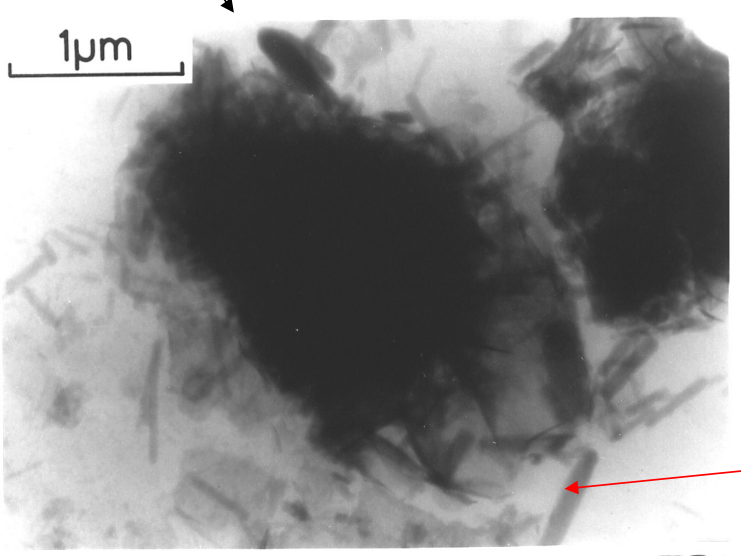
hydrogarnet



SEM
Thesis
Minard
2003

$C_3A + CaSO_4H_x$





Le ralentissement de réaction est liée à l'absorption des ions sulfates sur le surface du C_3A

$C_3A + CaSO_4H_x$

$$C_3A + 3C\bar{S}H_2 + 26H \Rightarrow C_3A.3(C\bar{S}).H_{32}\,(\text{ettringite})$$

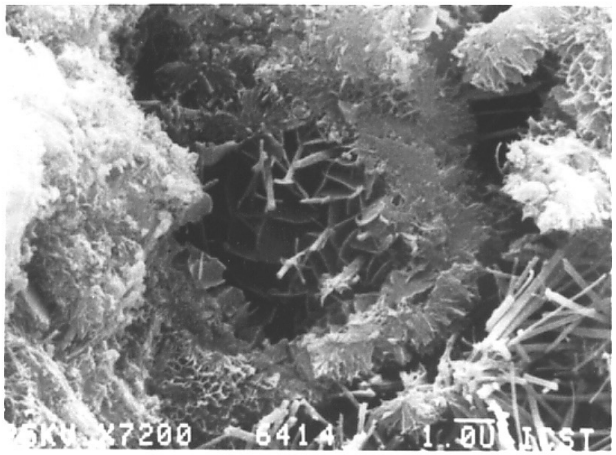
$$6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$$

$$\Rightarrow C_3A.3(C\bar{S}).H_{32}\,(\text{ettringite})$$

Épuisement du sulfate

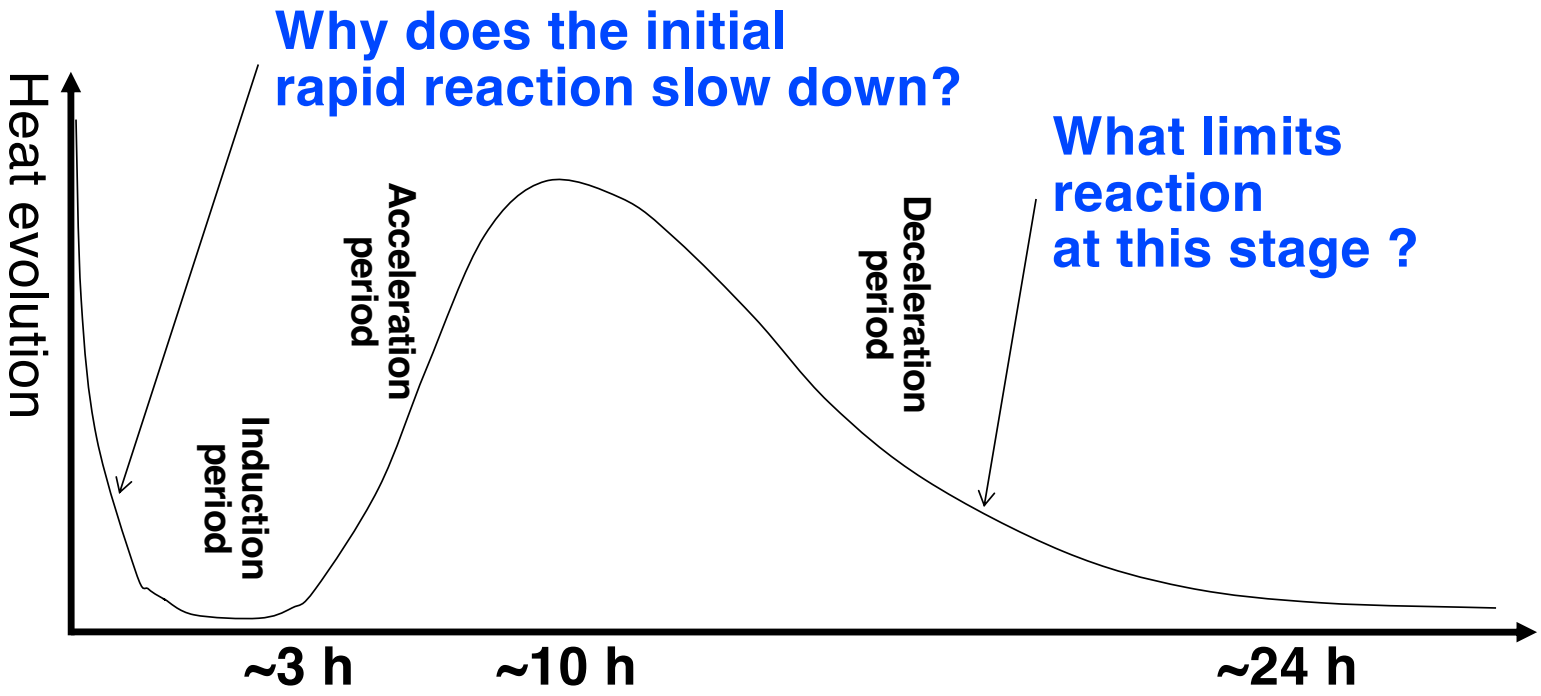
$$2C_3A + C_3A.3(C\bar{S}).H_{32} + 4H \Rightarrow 3C_3A.C\bar{S}.H_{12}$$

Calcium monosulfo aluminate
Monosulfo aluminate de calcium
"AFm"

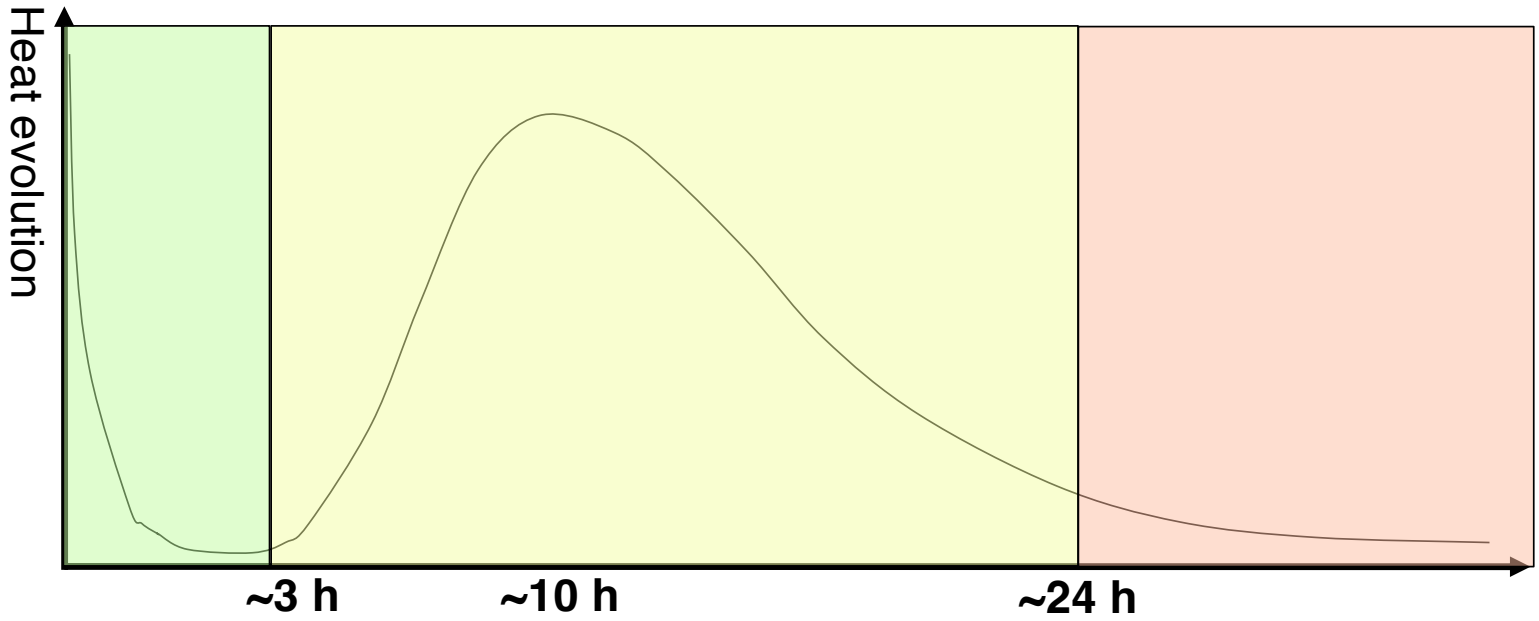


Pâte à 7 jours
Formation local de monosulfo à l'intérieur des couches de C-S-H ou il y a du C_3A disponible.
L'ettringite reste à l'extérieur du grain.

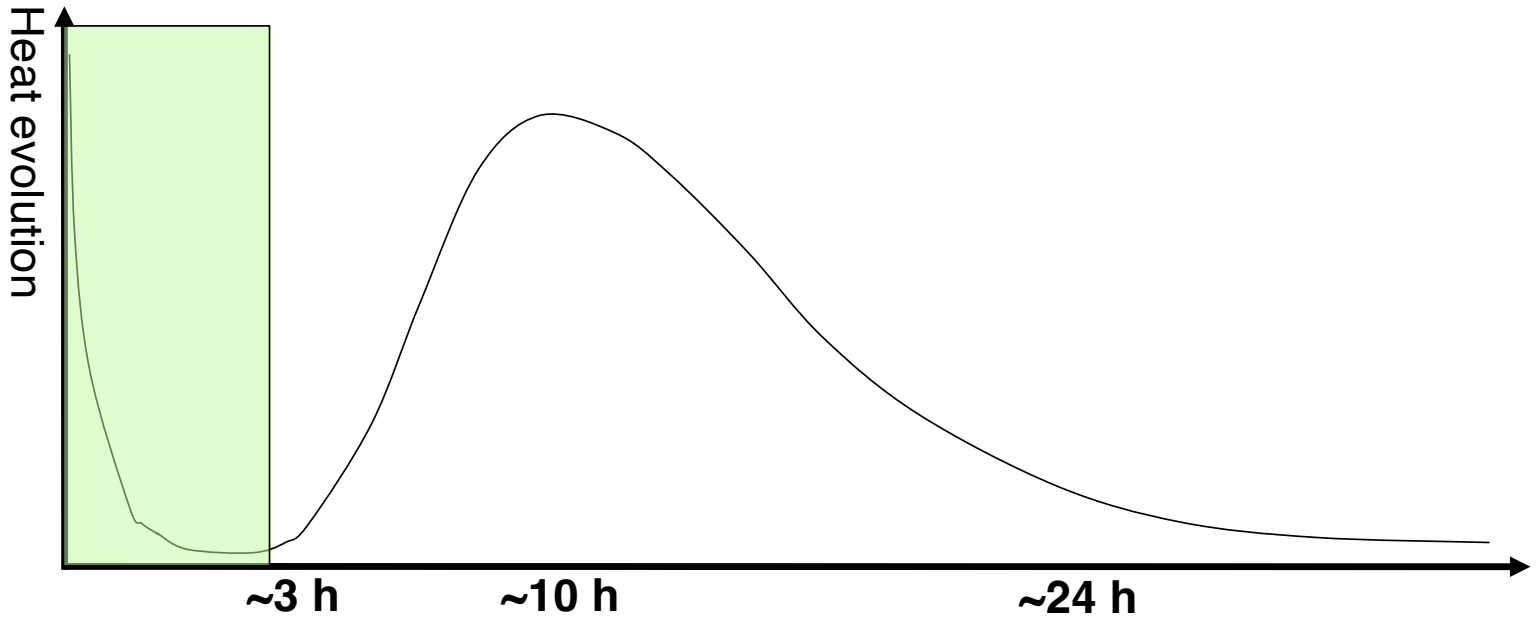
underlying mechanisms



Three periods



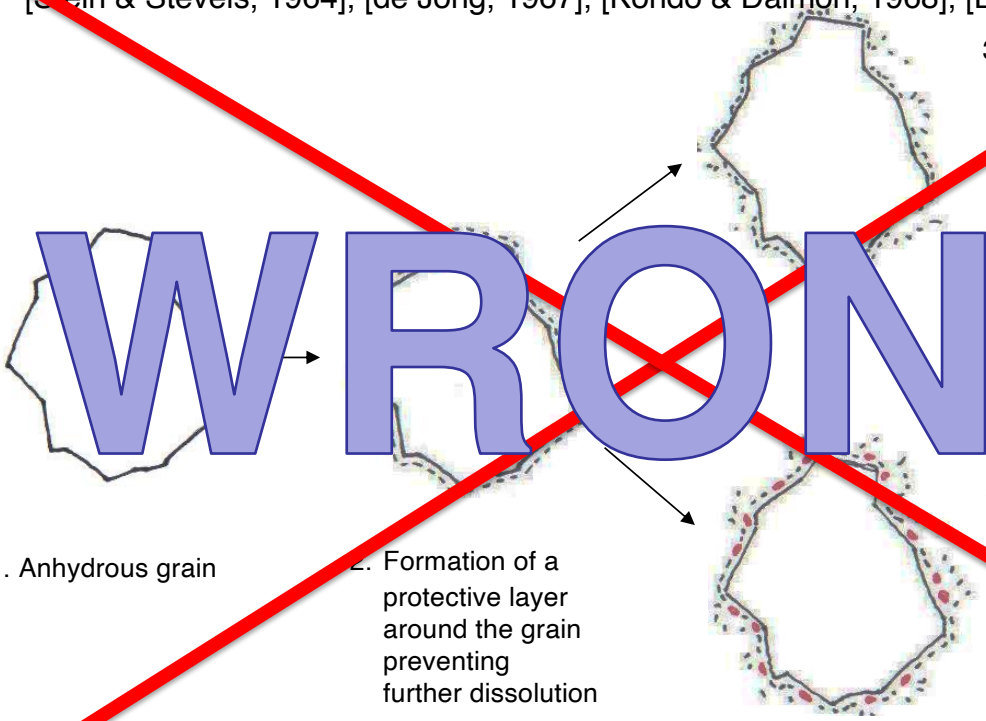
Induction period



Most wide spread idea

A) PROTECTIVE MEMBRANE THEORY

[Stein & Stevels, 1964], [de Jong, 1967], [Kondo & Daimon, 1968], [Brown et al. 1985]



1. Anhydrous grain

2. Formation of a protective layer around the grain preventing further dissolution

3.a) Disruption of the protective layer by osmotic pressure due to the difference of ion concentration between the inner solution and the pore solution creating an osmotic pressure.

[Double et al., 1980]

3.b) Disruption of the protective layer due to the nucleation and growth of more stable hydrates in the protective membrane

[Stein & Stevels, 1964]
[Gartner & Jennings, 1987]

WRONG!

No direct evidence

Portland cement observed in the cryo SEM

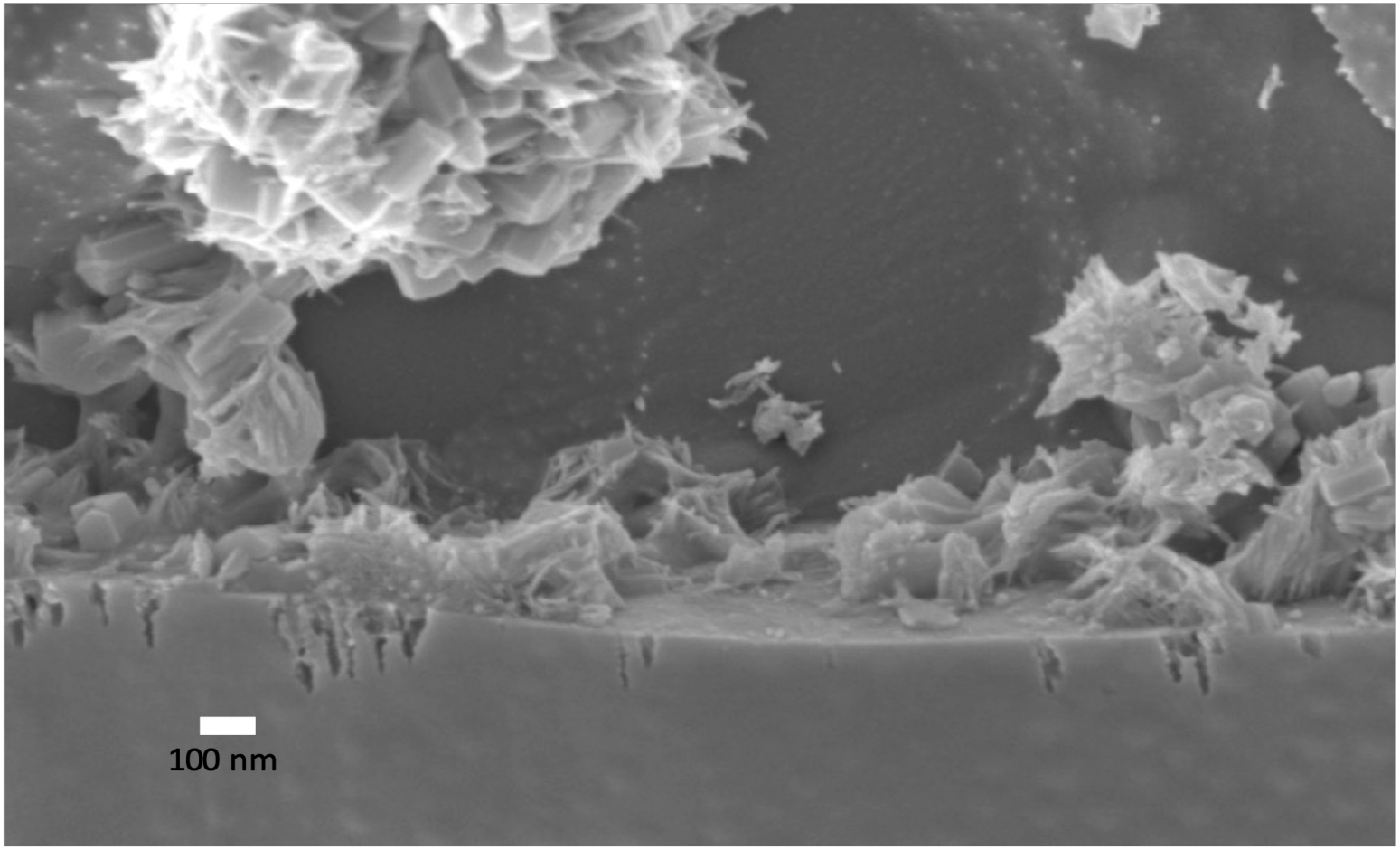
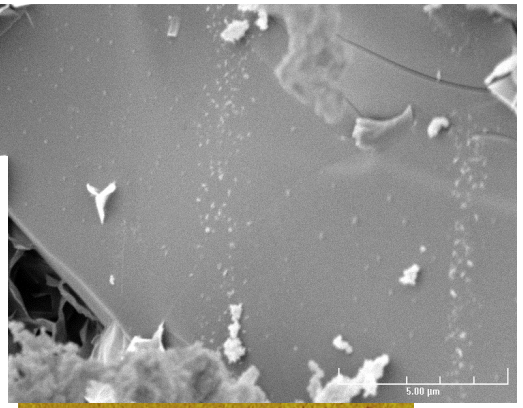


Image from Luc Nicoleau

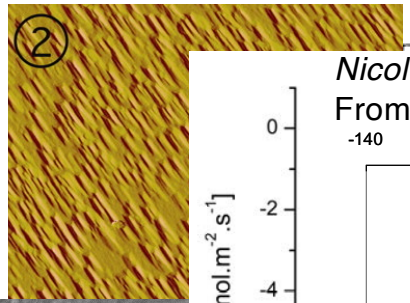
Theories of dissolution from Geochemistry

dissolution as negative growth

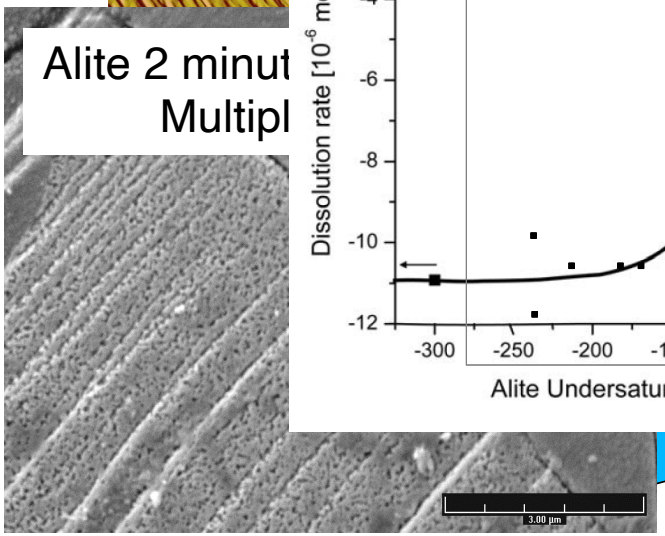
2 minutes in saturated lime sol.
Smooth surface

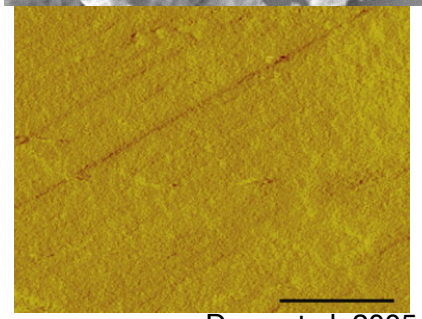


Dove et al. 2005



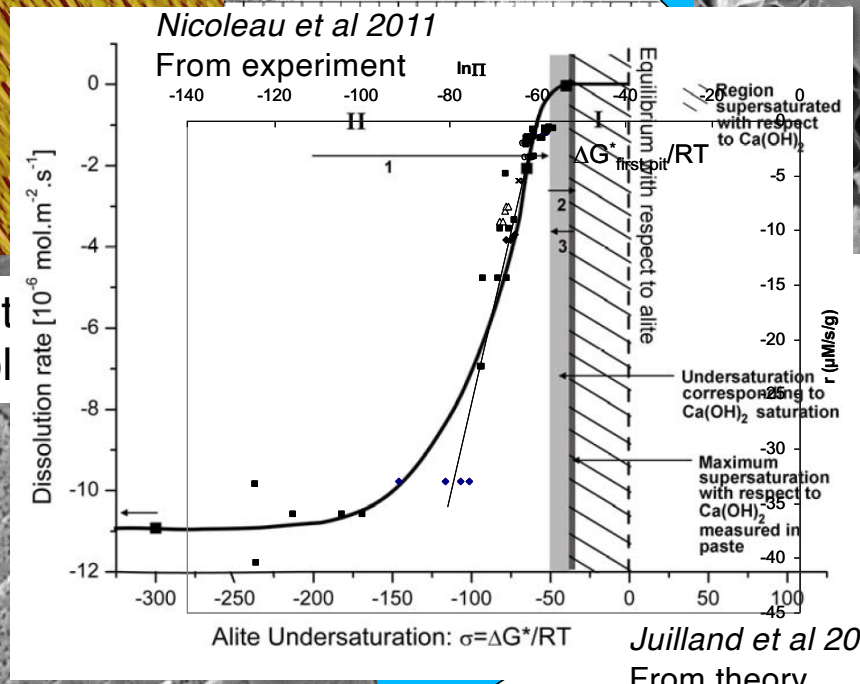
Alite 2 minut
Multipl





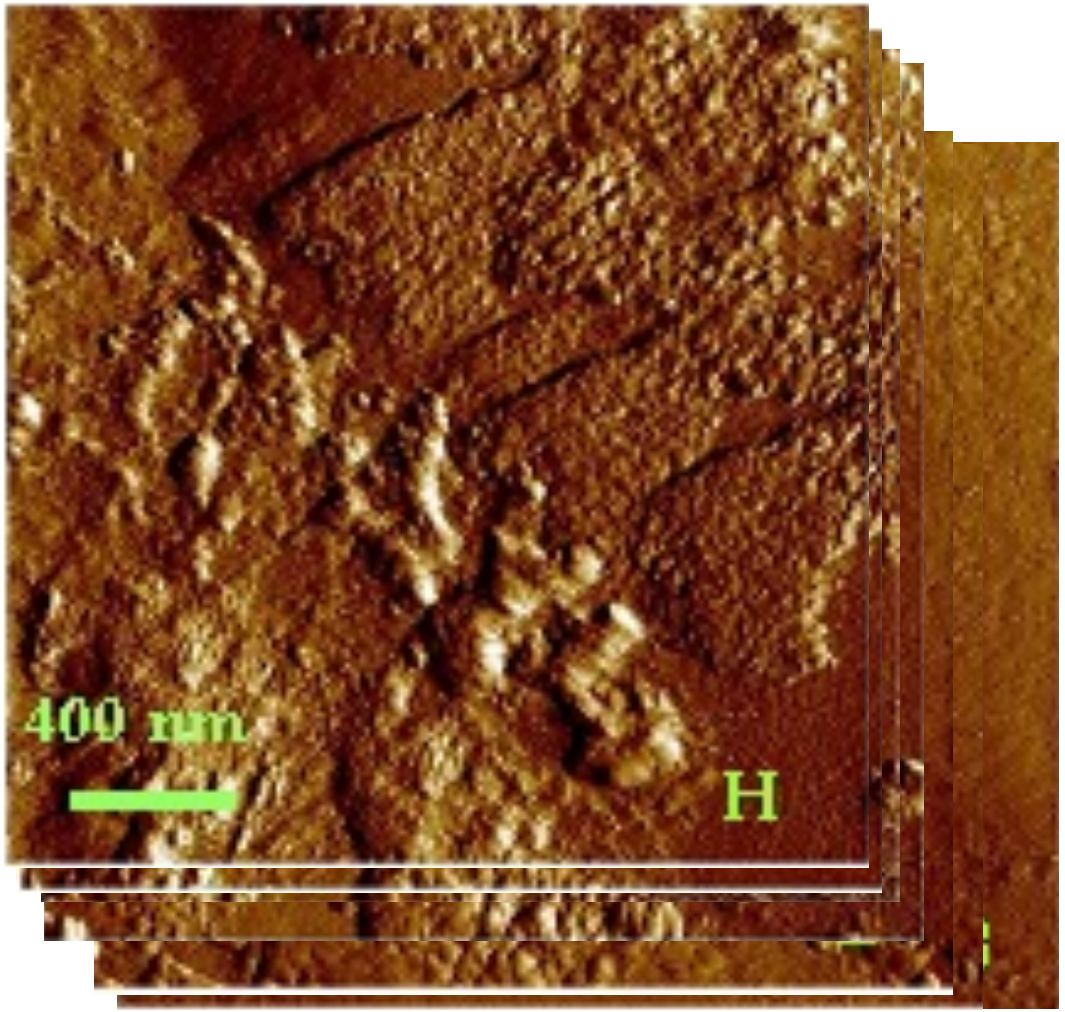
Dove et al. 2005

Nicoleau et al 2011
From experiment



Juilland et al 2009
From theory

AFM wet cell



Thesis Helène di Murro U. Bourgogne

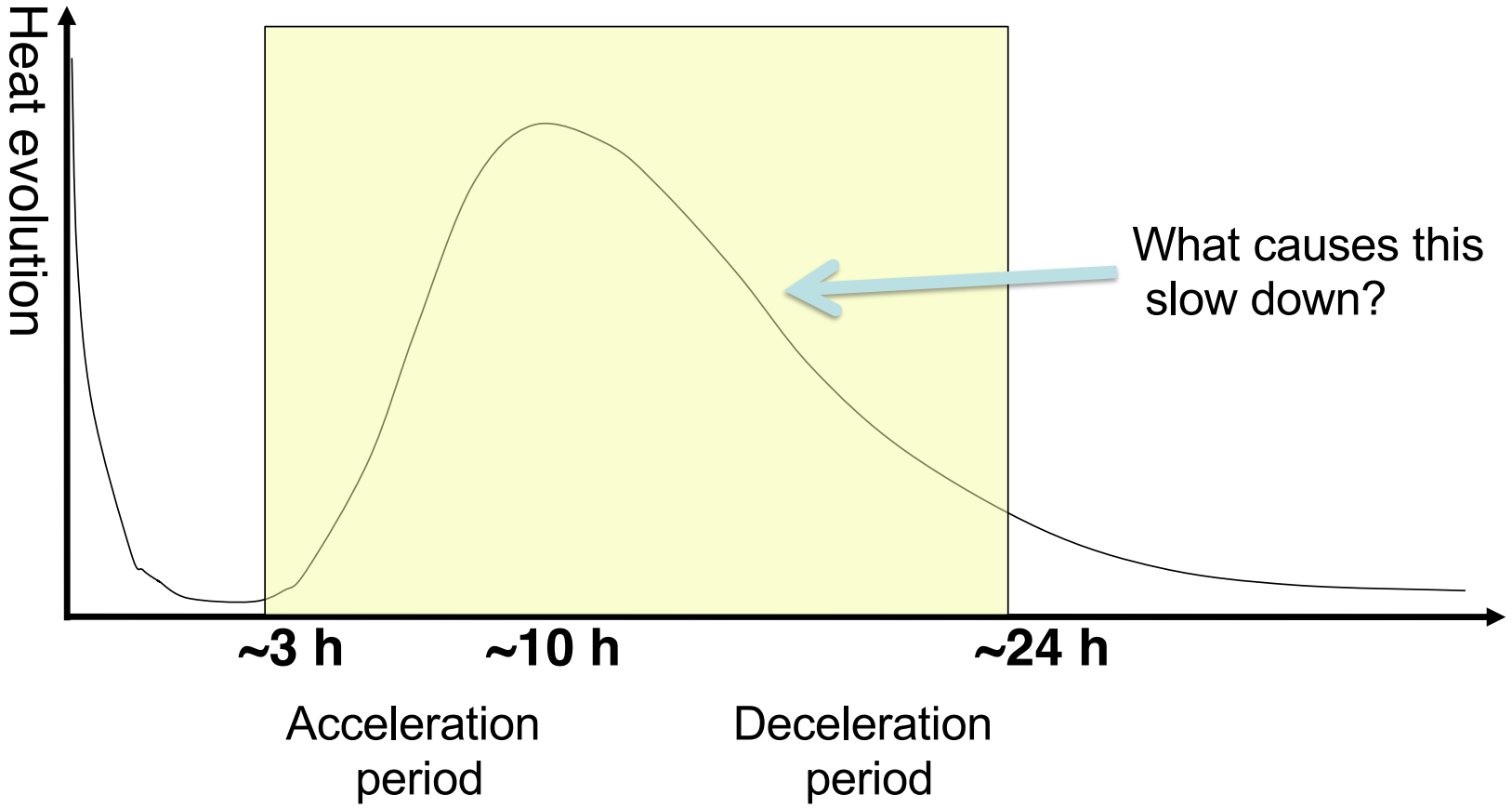
Induction period, summary

- No evidence for protective layer,
  cannot explain many experimental results

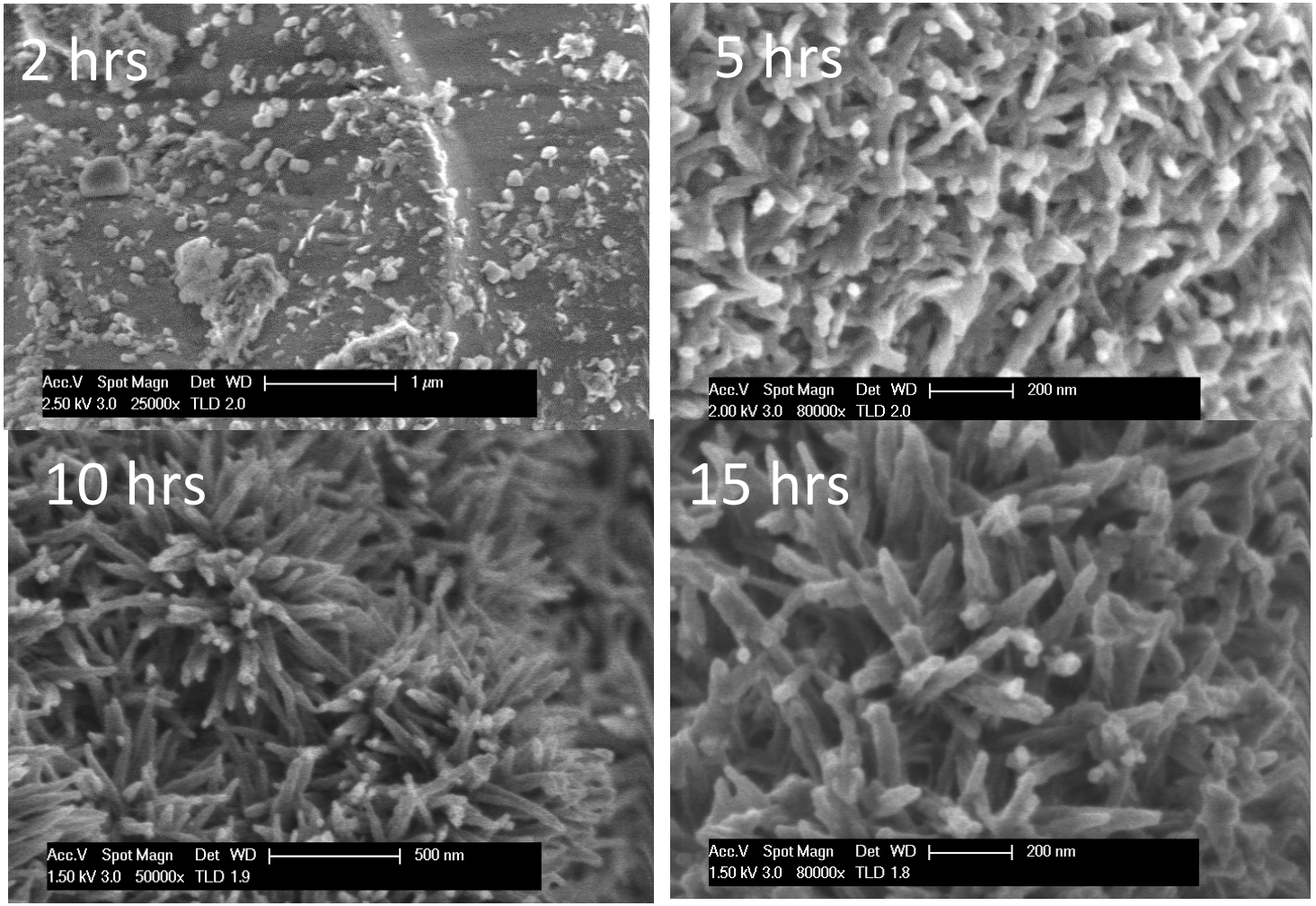
- Dissolution as a function of undersaturation:
  - Based on solid theoretical foundation from geochemistry;
  - Excellent agreement between, theory, experimental measurement of dissolution and modelling;
  - Can explain all experimental observations.

The Main Hydration Peak

Period II, main heat evolution peak



End of induction period: growth of C-S-H (& CH)



Berodier 2015

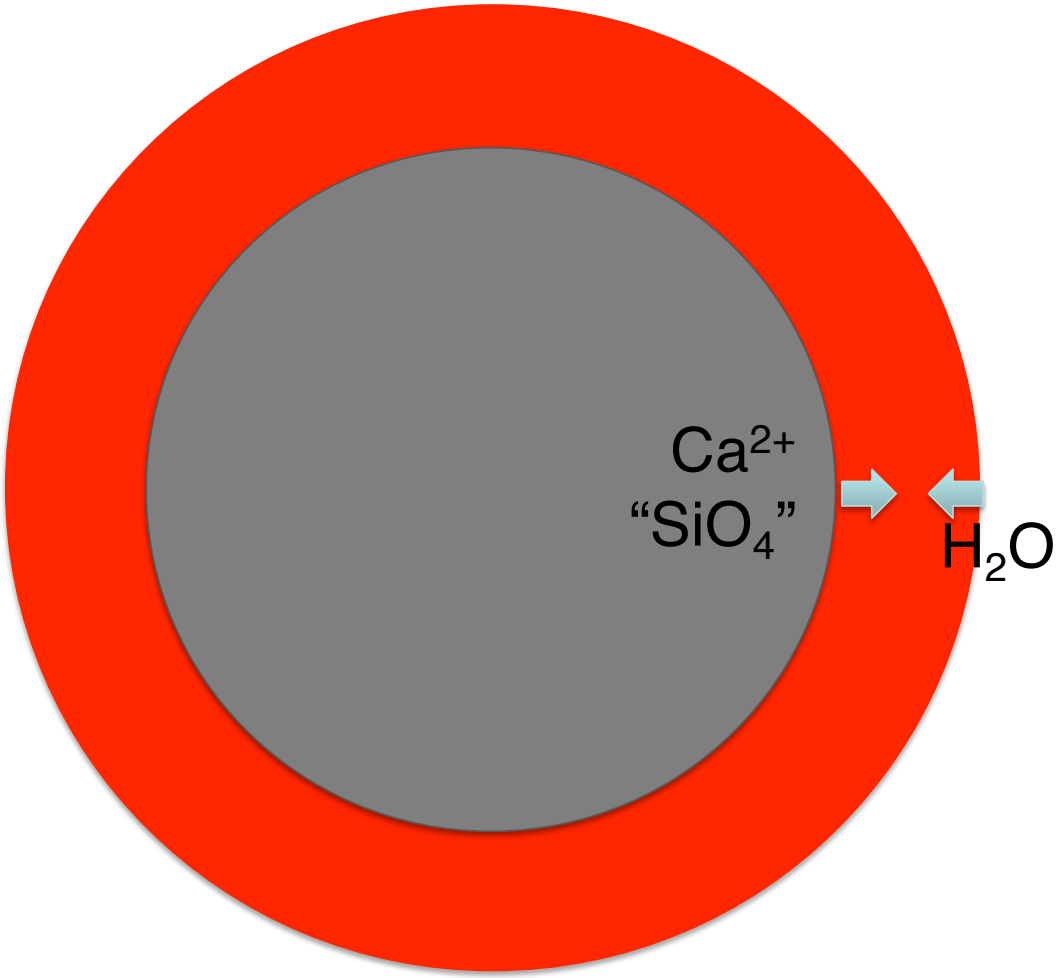
Beware of fitting!

- At least 4 very different mechanisms have been fitted to the data set of Costoya!
- They cannot all be right!
- Get 4 pictures from papers

Main hypotheses for slow down

- Diffusion controlled through layer
- Impingement of product
- Neither of these
  is supported by the experimental data

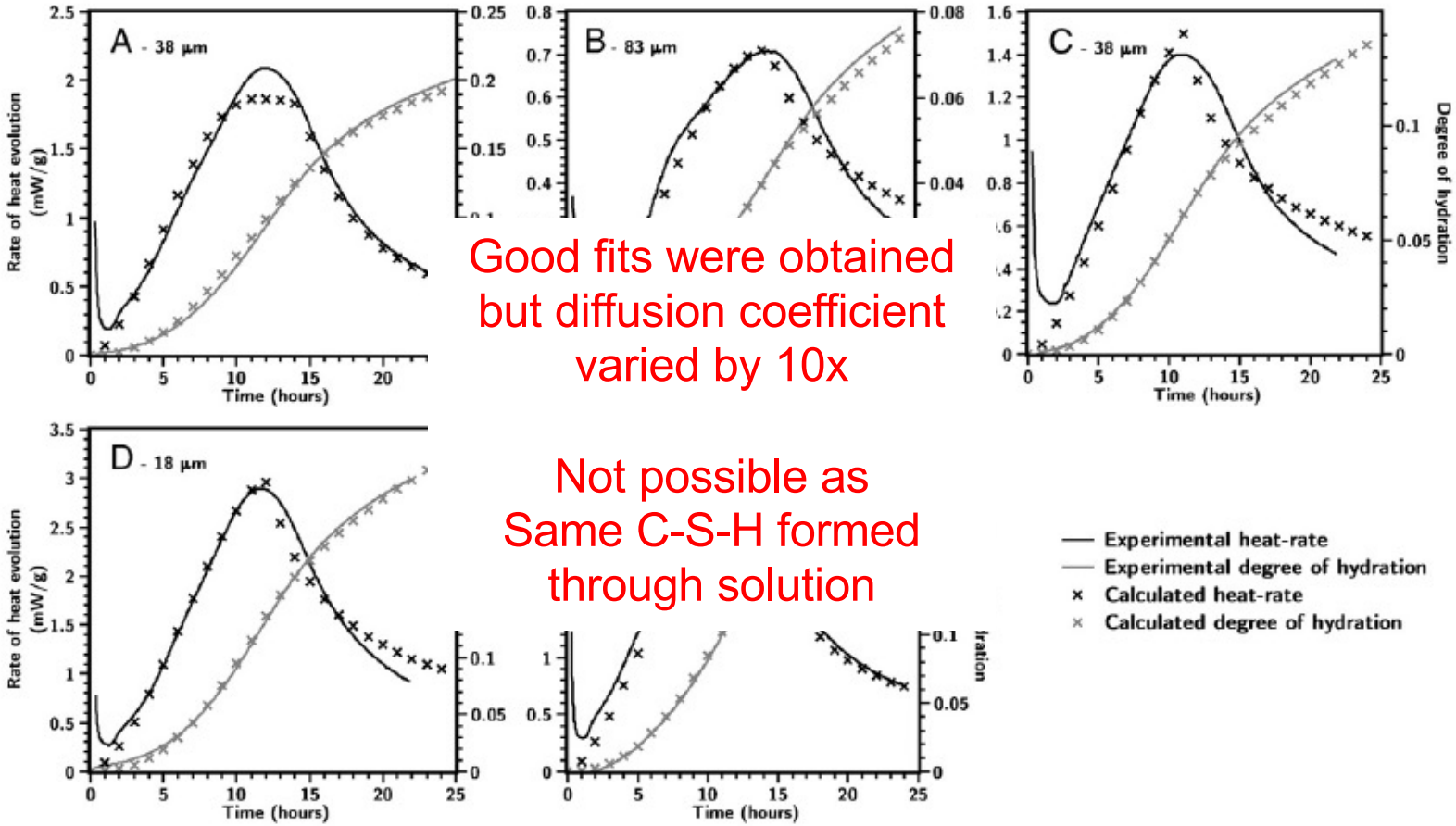
Diffusion



The layer of hydration products provides a barrier to the reaction.

Rate limiting step is the diffusion of species through this layer

Bishnoi 2008 : Post-peak “Diffusion”

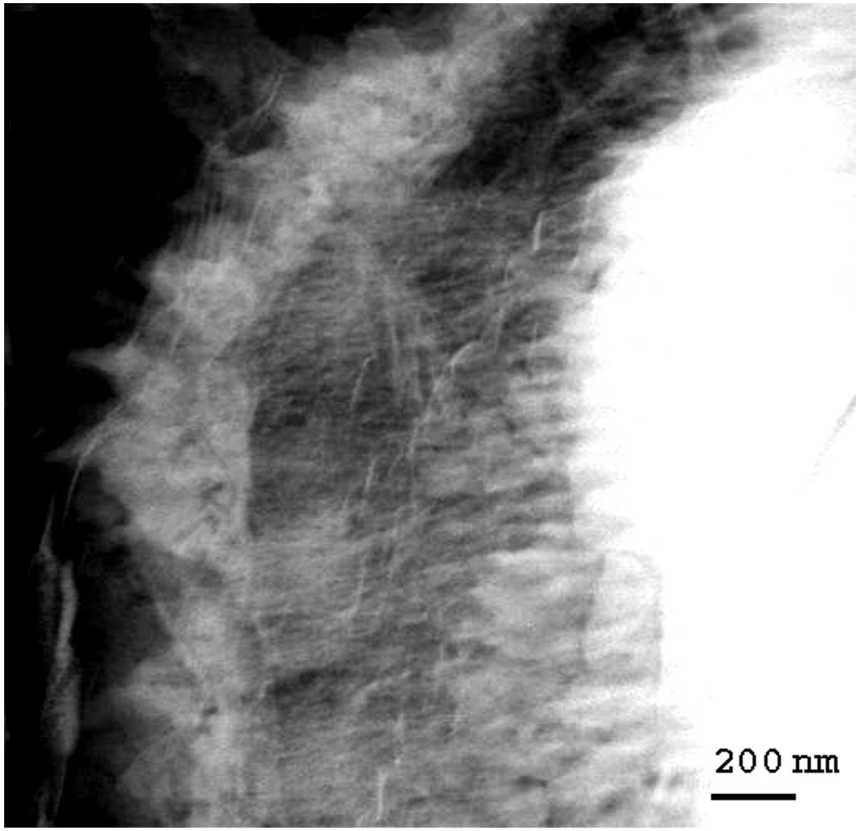


Good fits were obtained but diffusion coefficient varied by 10x

Not possible as Same C-S-H formed through solution

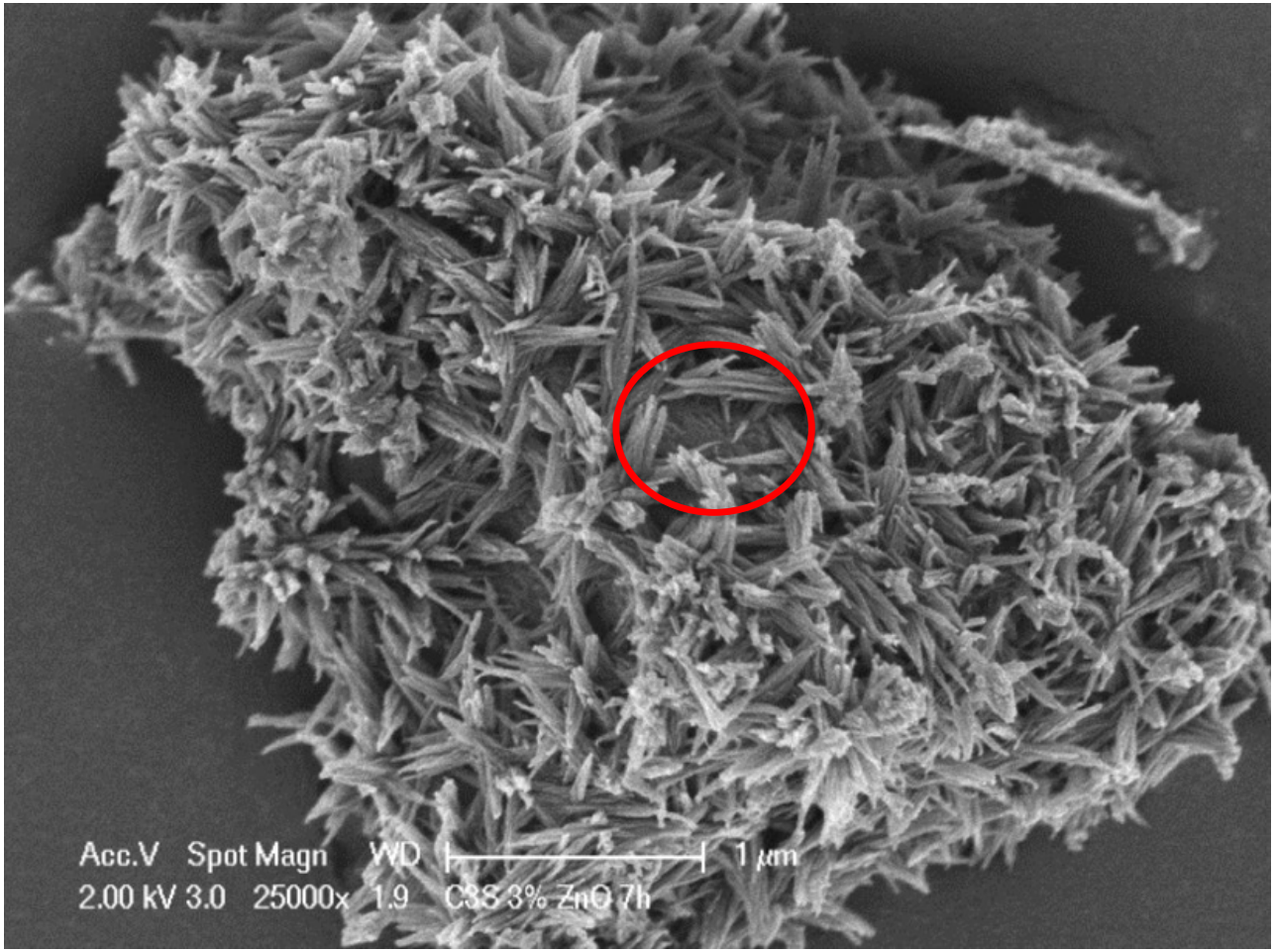
Evidence against diffusion

- Same C-S-H for different particle sizes, why should diffusion coefficient vary by 10X
- Success of maturity approaches: same activation energy throughout main hydration peak
  - Bond breaking / making processes typically have Ea > 40 kJ/mol
  - Transport controlled processes have Ea <~20 kJ/mol
- Low density region inside “shell” does not fill in until much later

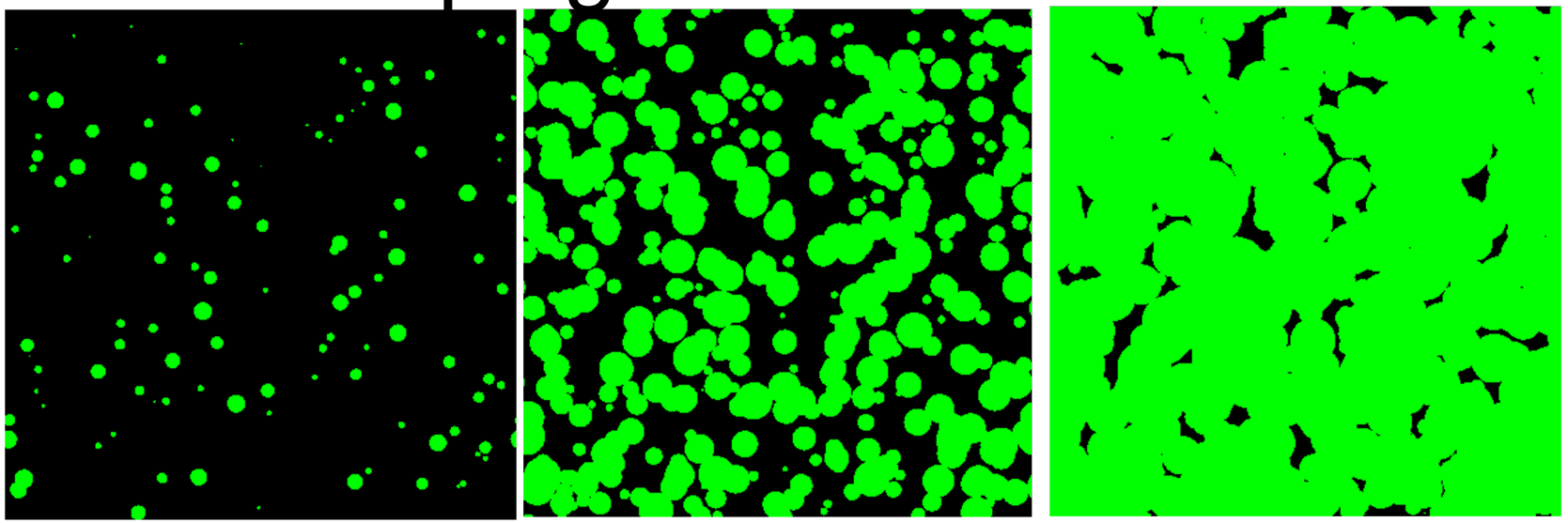


Gallucci et al. 2010

The “layer” is incomplete



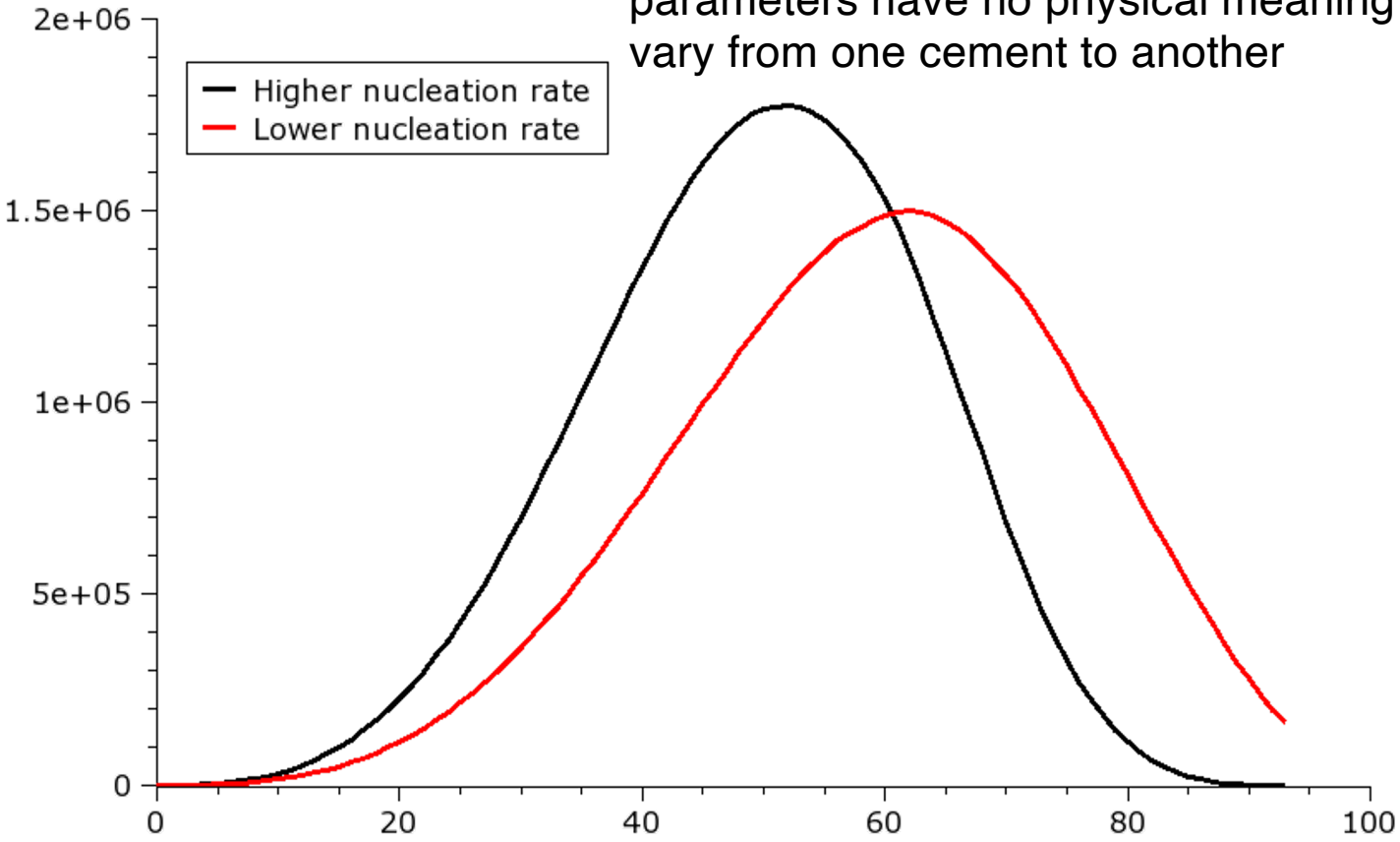
Impingement: Avrami



Developed for solidifying metals
Simple 3D nucleation and growth:
growth $\propto$ surface available

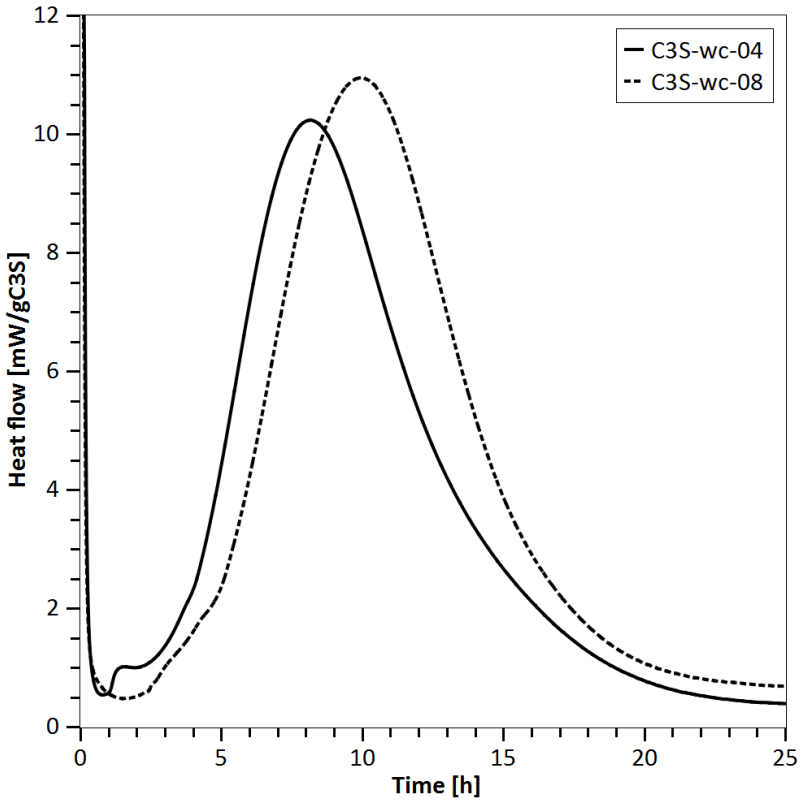
Avrami equation gives the right kind of peak

It can be FITTED to cement hydration, but parameters have no physical meaning and vary from one cement to another

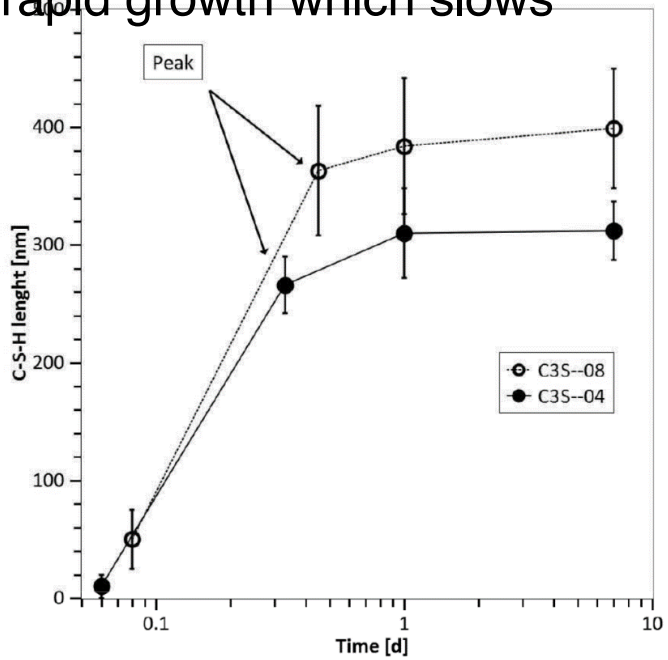


Impact of w/c

- Very low impact of W/C
  – this negates impingement as possible cause for deceleration

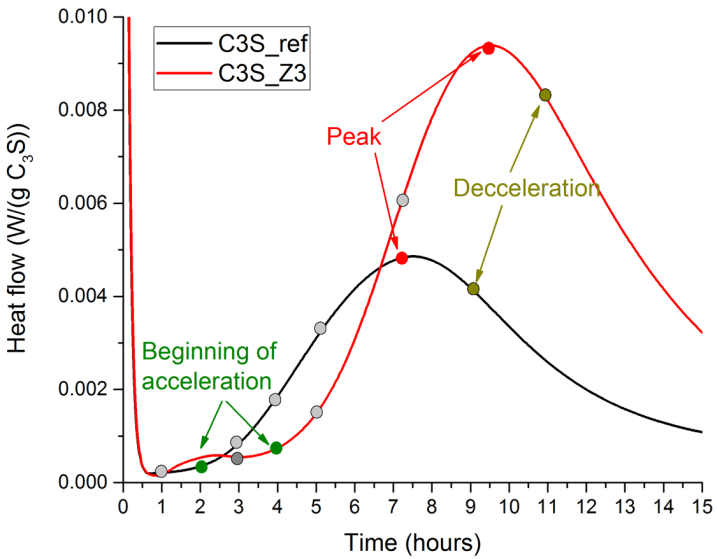


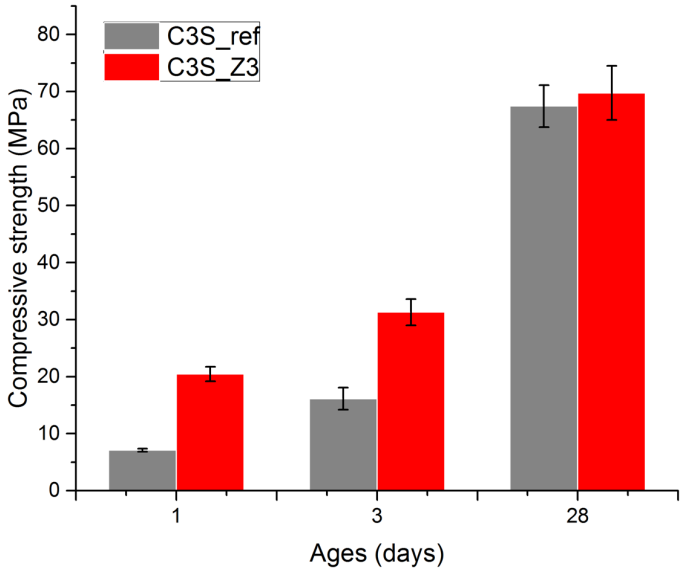
Measurement of length of C-S-H needles shows initial rapid growth which slows



Bazzoni 2014

Small concentrations of zinc, huge impact on main peak

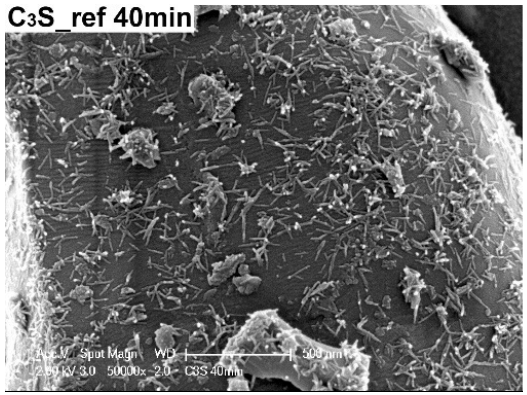


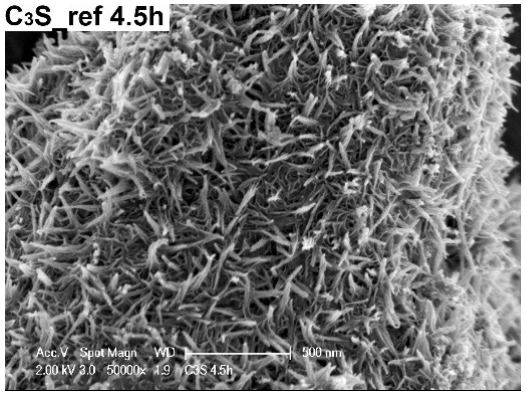


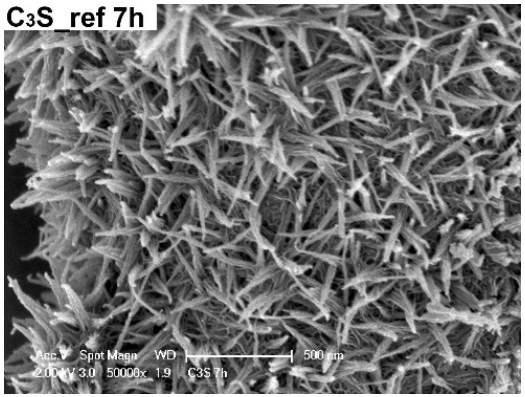
Micro mortar ($2x2x2cm^3$) compressive strength

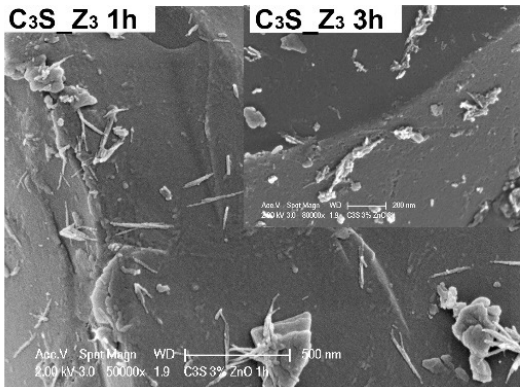
Growth of C-S-H “needles”, dramatic effect of Zn

Induction period | **Acceleration period** | **Peak**

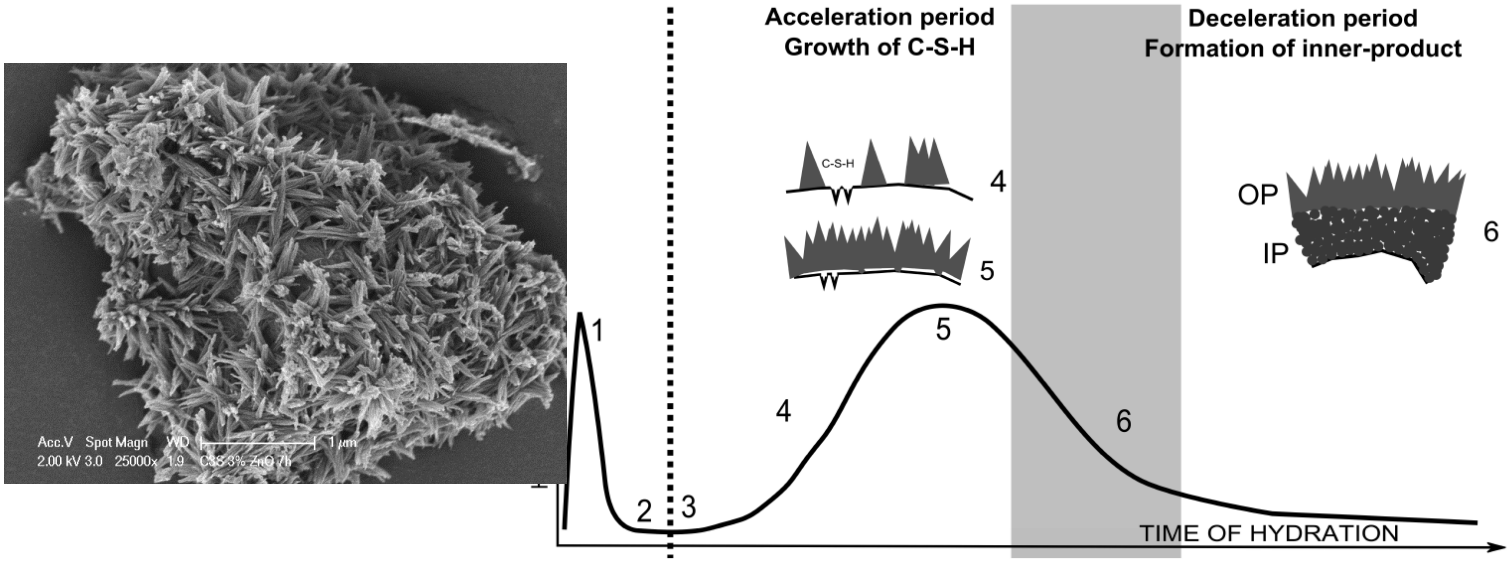








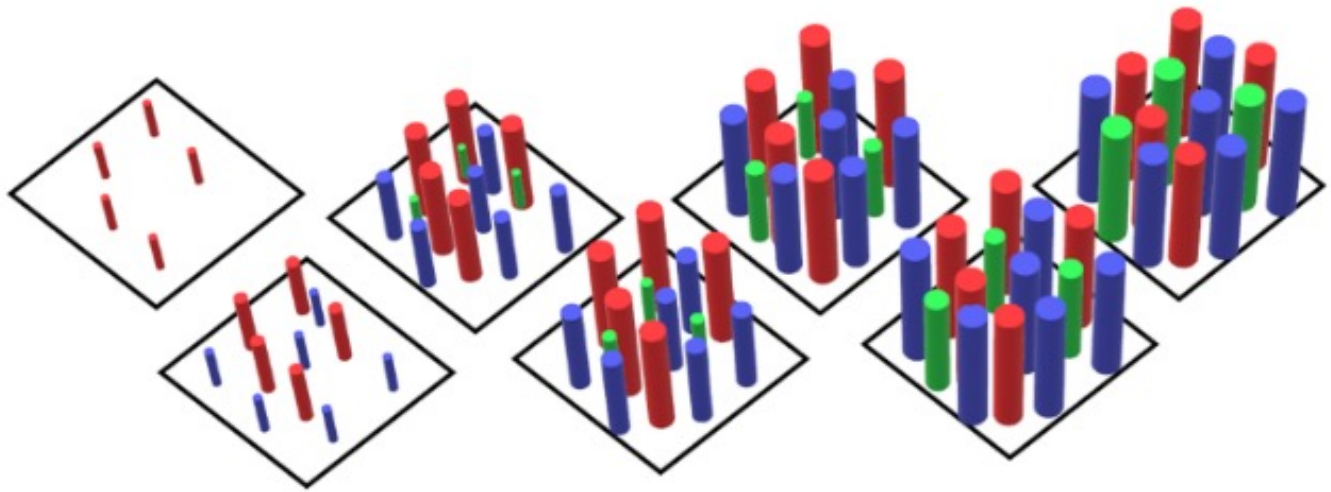
Bazzoni's scenario



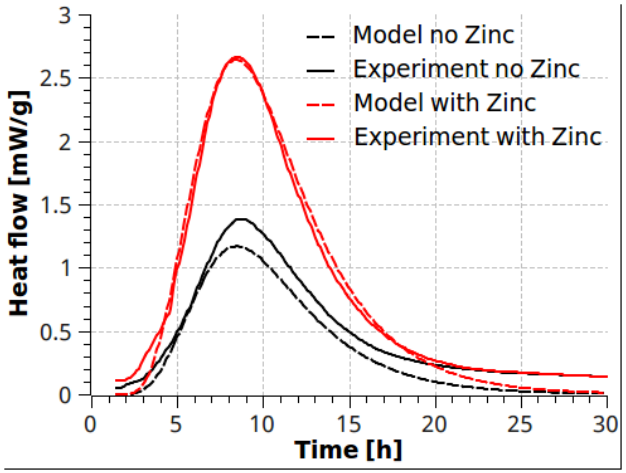
- Needles gradually cover the surface during the acceleration period.
- Needles grow fast to a certain length and then the rate slows dramatically.

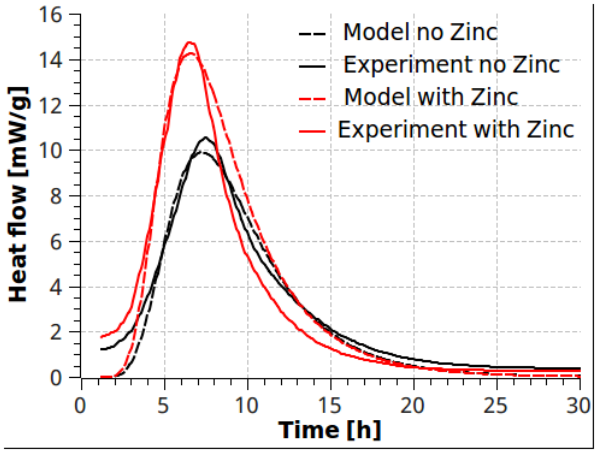
Needle model: Ouzia 2017

- C-S-H growth as needles
- ALL parameters from experiment – **NO fitting**



Needle model: Ouzia 2017



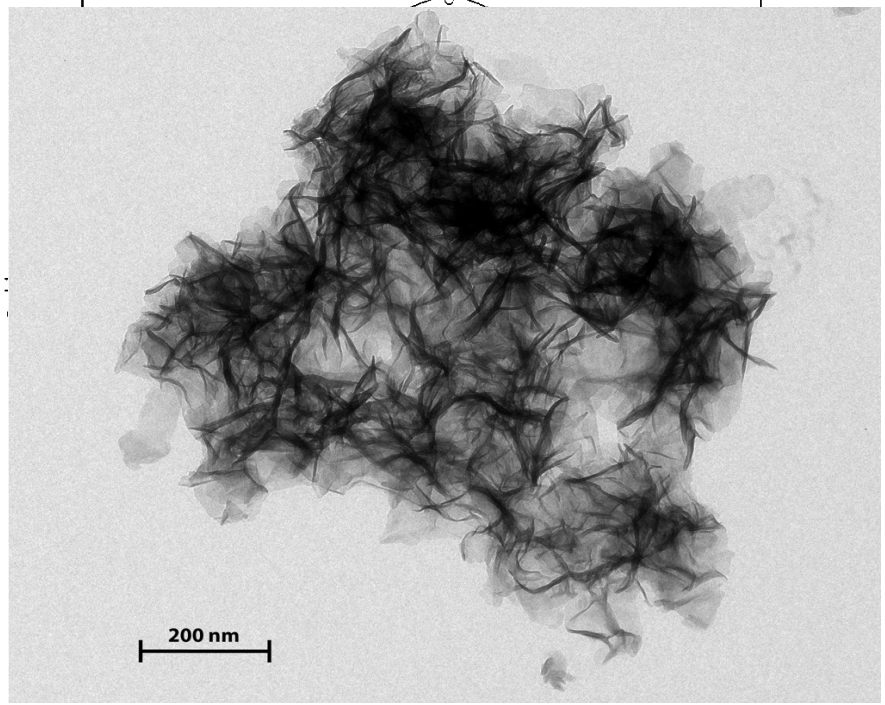


Open question?

- If mechanism is C-S-H growth: What controls this?

  Solution composition ?

  Build up of defects?

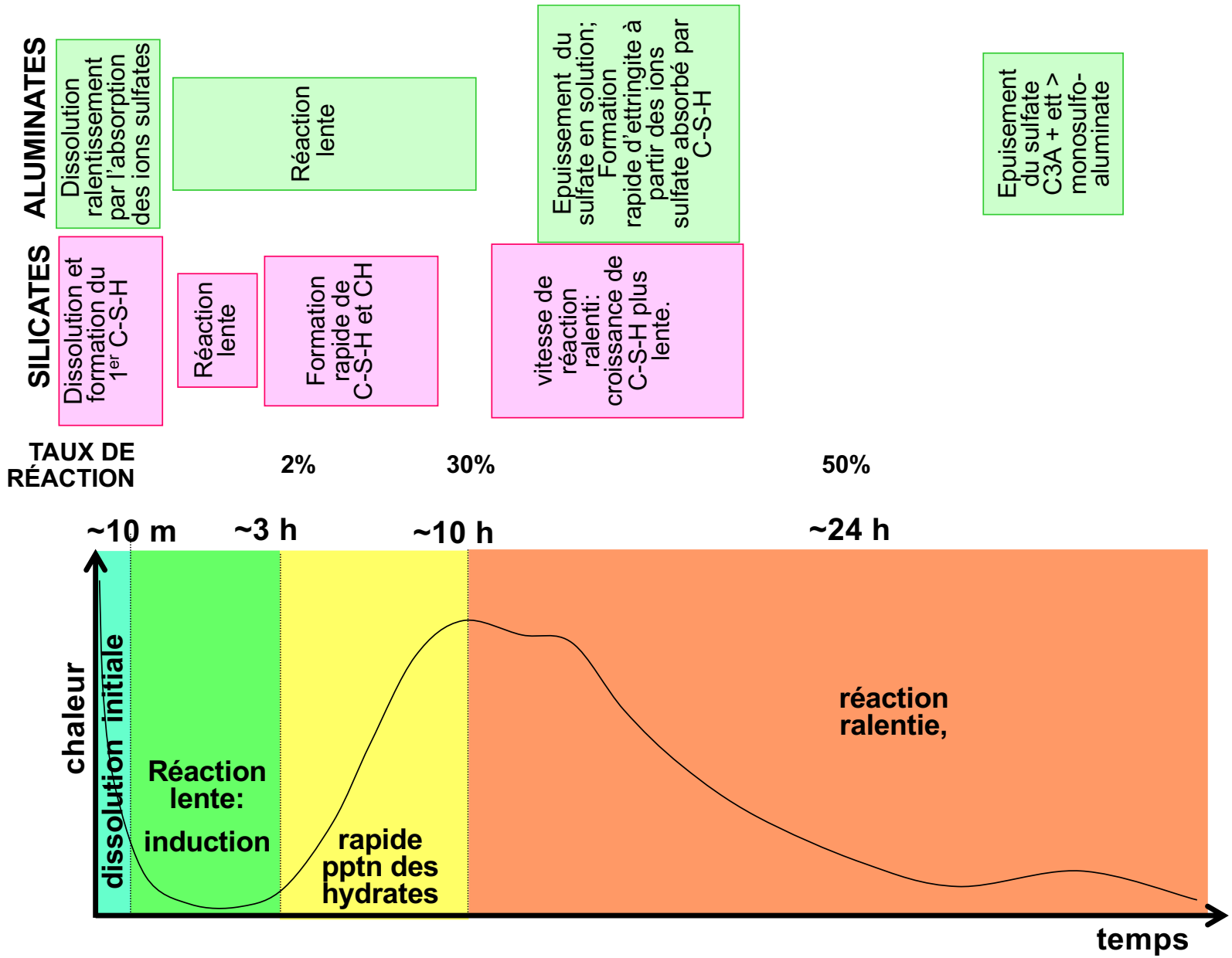


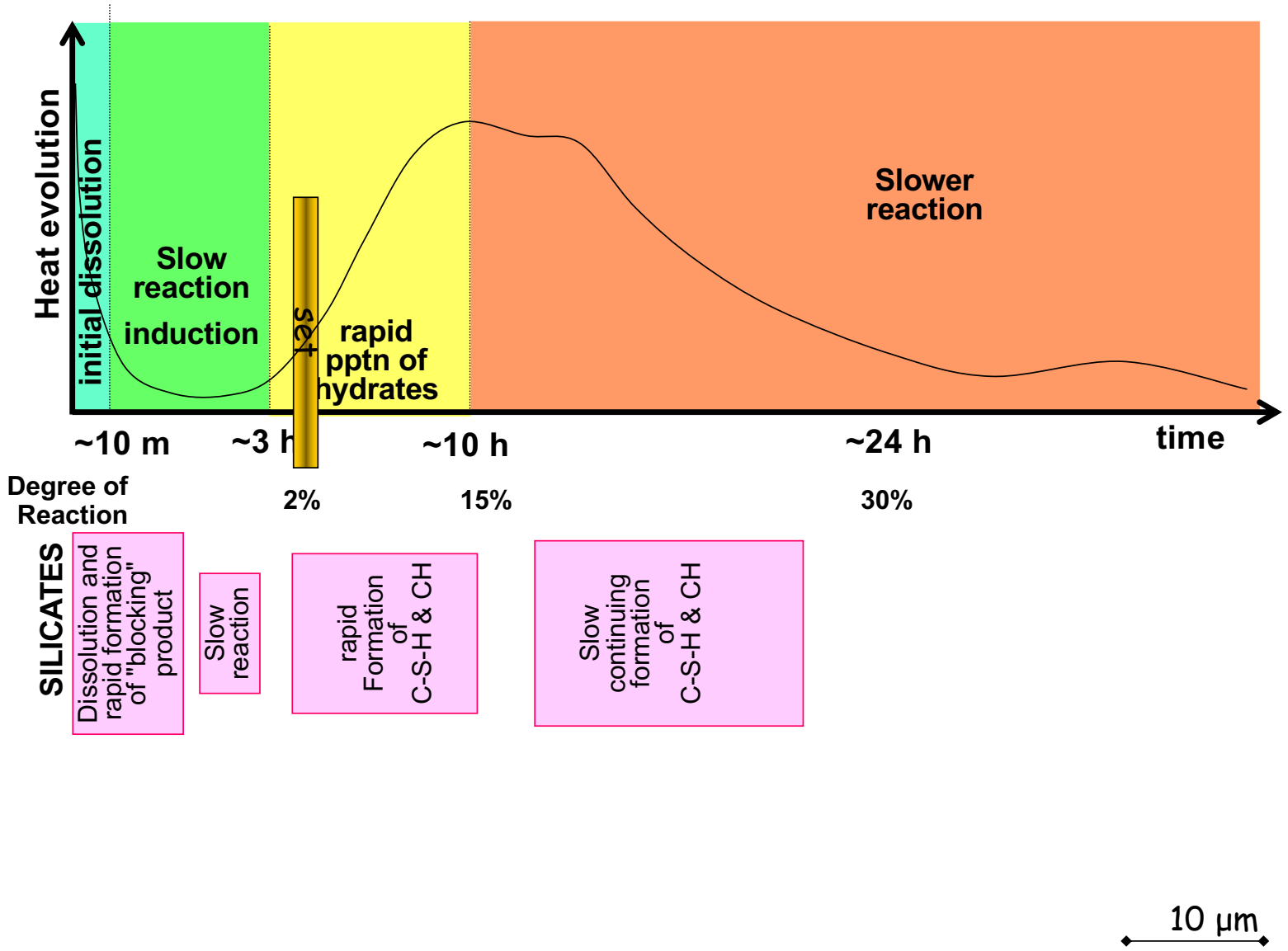
Other?

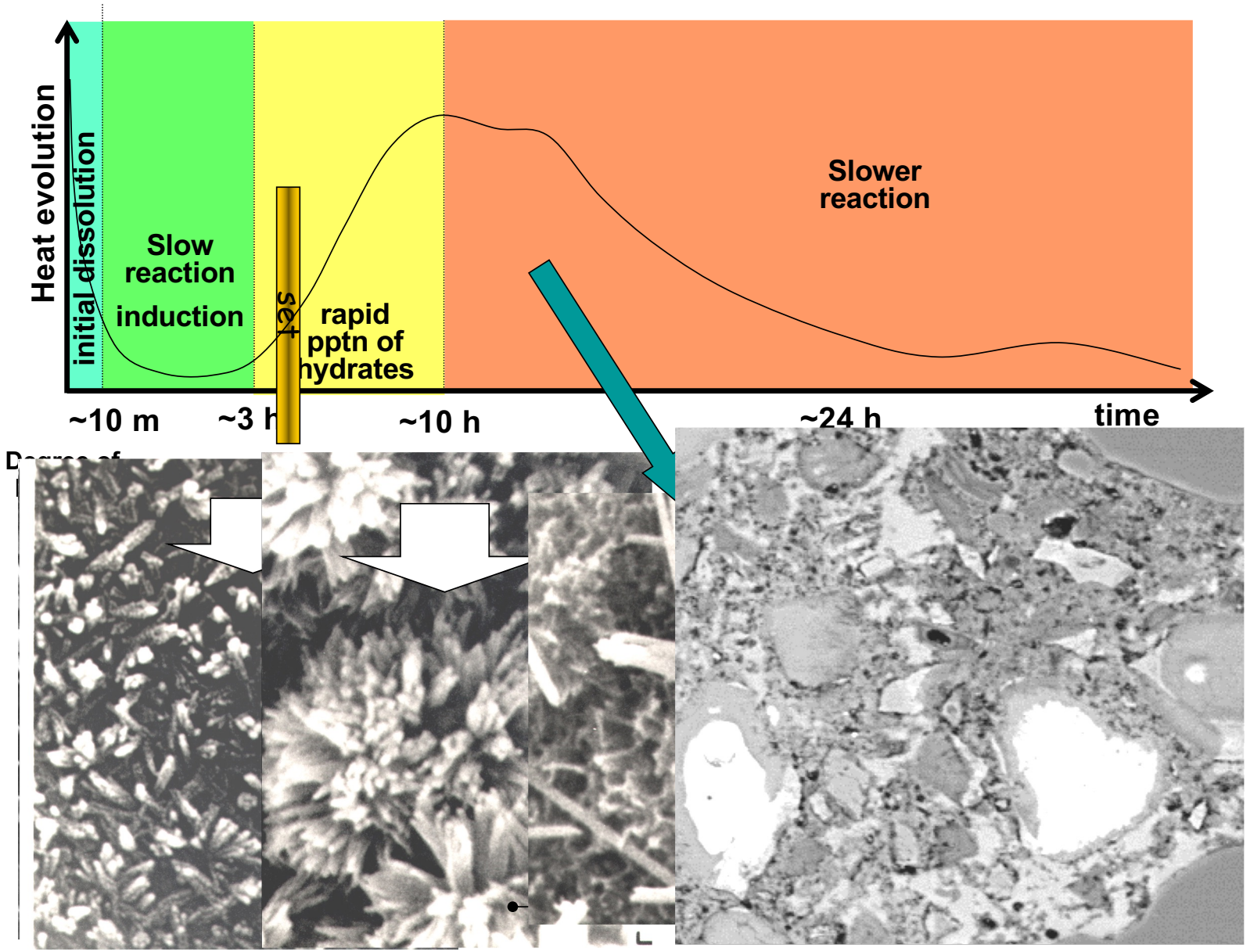
Main peak, summary

- Many hypotheses can fit the form of the peak
- Need to look at
  a wide range of variables and
  have physically measureable parameters
- Best hypothesis:
  Fast growth of needles to a critical length

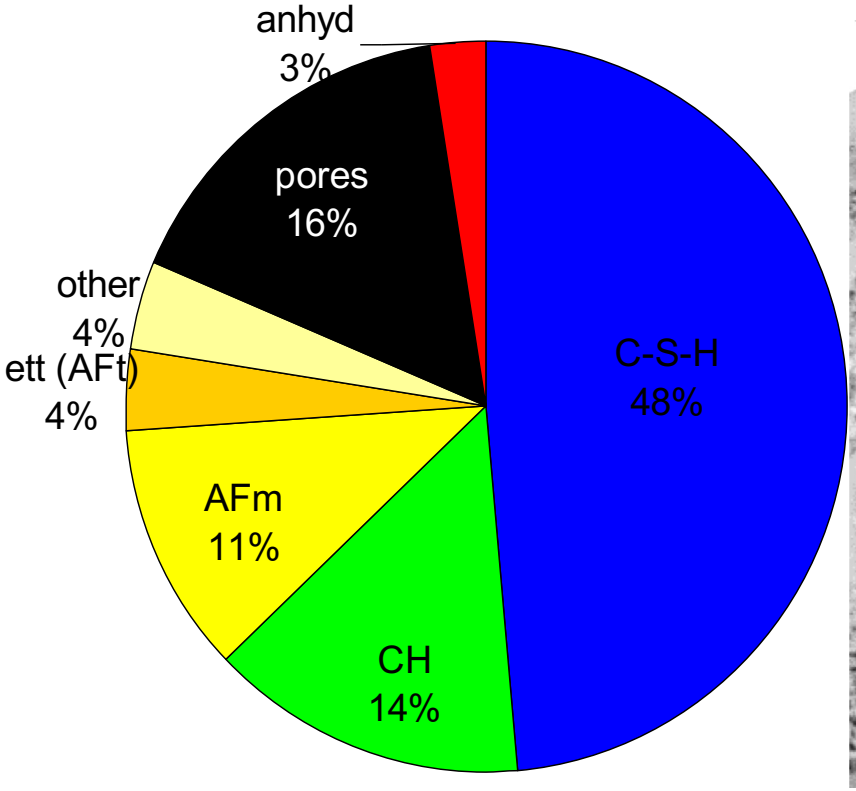
Résumé de l’hydratation

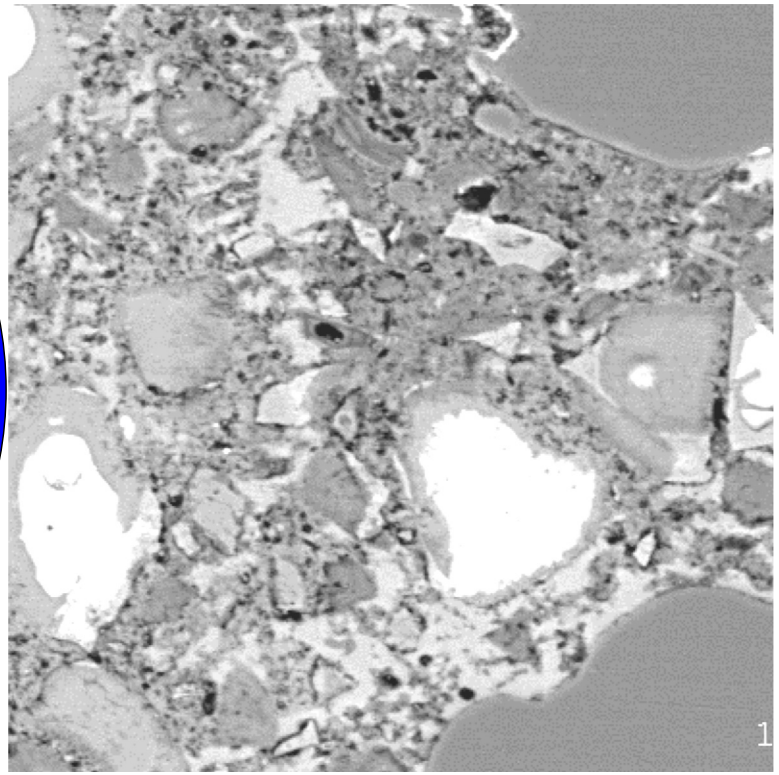

ALUMINATES
Dissolution ralentissement par l'absorption des ions sulfates
Réaction lente
Epuisement du sulfate en solution; Formation rapide d'ettringite à partir des ions sulfate absorbé par C-S-H
Epuisement du sulfate C3A + ett > monosulfo-aluminate
SILICATES
Dissolution et formation du 1er C-S-H
Réaction lente
Formation rapide de C-S-H et CH
vitesse de réaction ralenti: croissance de C-S-H plus lente.
TAUX DE RÉACTION
2%
30%
50%
~10 m
~3 h
~10 h
~24 h
chaleur
dissolution initiale
Réaction lente:
induction
rapide pptn des hydrates
réaction ralentie,
temps


Heat evolution
initial dissolution
Slow reaction
induction
set
rapid pptn of hydrates
Slower reaction
~10 m
~3 h
~10 h
~24 h
time
Degree of Reaction
2%
15%
30%
SILICATES
Dissolution and rapid formation of "blocking" product
Slow reaction
rapid Formation of C-S-H & CH
Slow continuing formation of C-S-H & CH
10 µm


Heat evolution
initial dissolution
Slow reaction
induction
set
rapid pptn of hydrates
Slower reaction
~10 m
~3 h
~10 h
~24 h
time

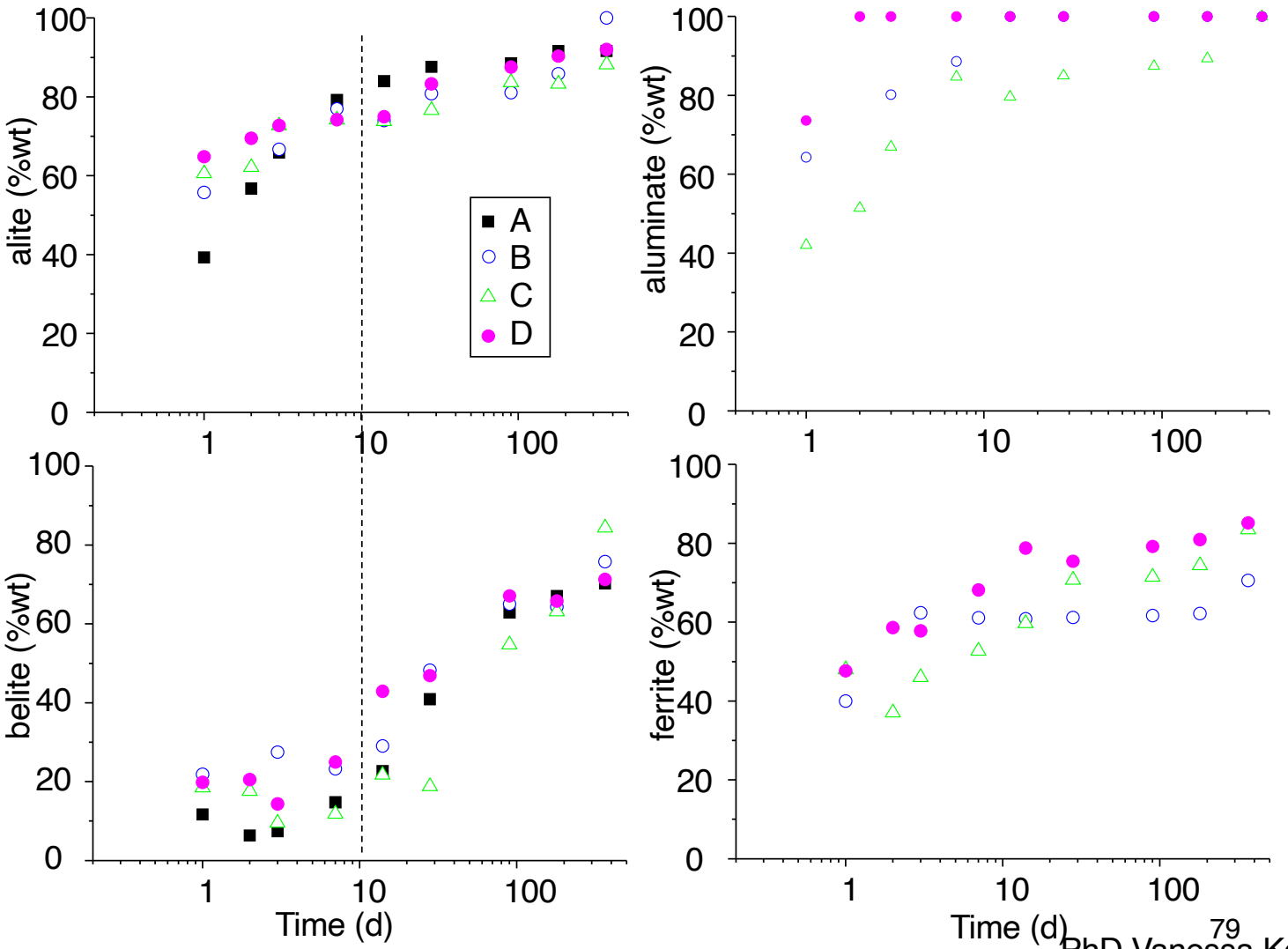
Bilan Volumétrique





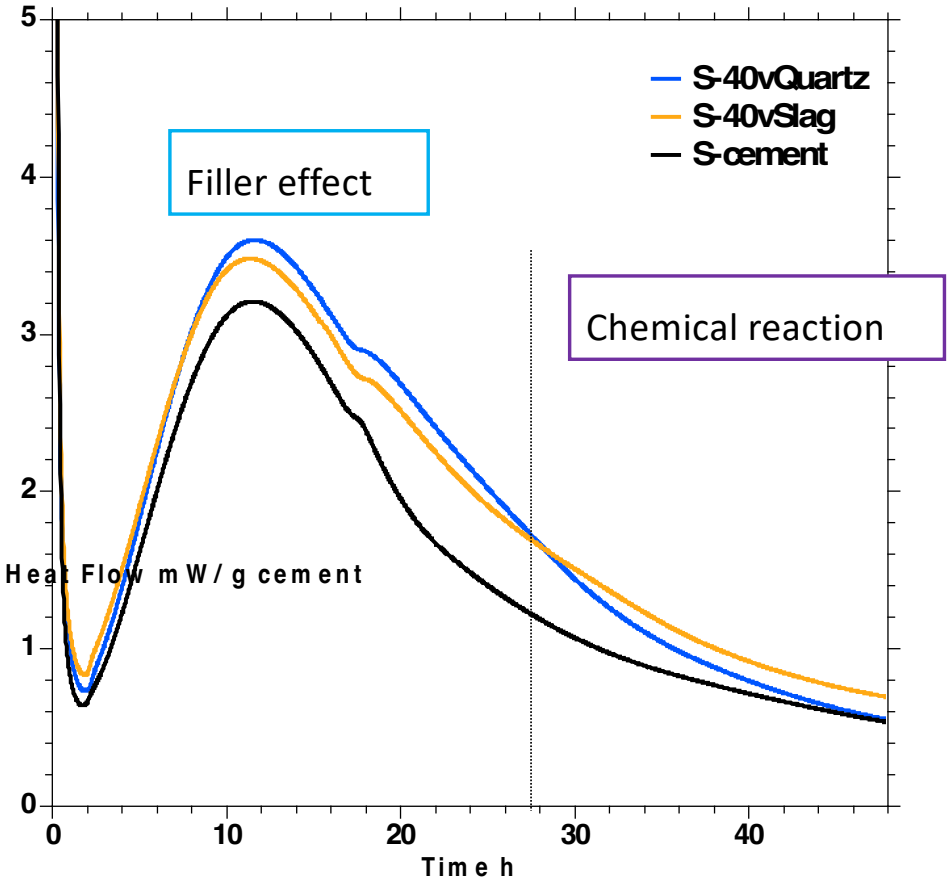
Pâte de ciment Portland, e/c = 0,5, 14 mois

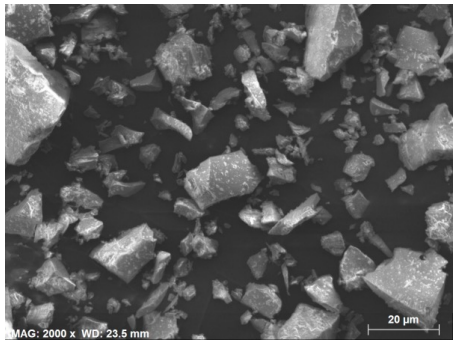
Experimental observations of reaction of different components



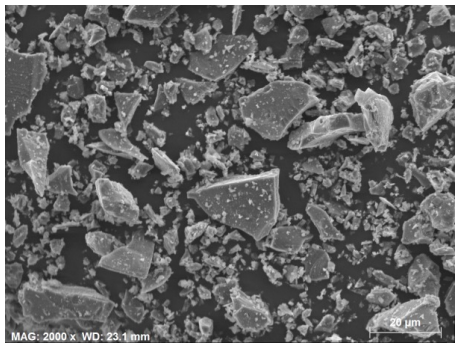
Impact of SCMs
on main heat evolution peak

Physical effect on main hydration peak





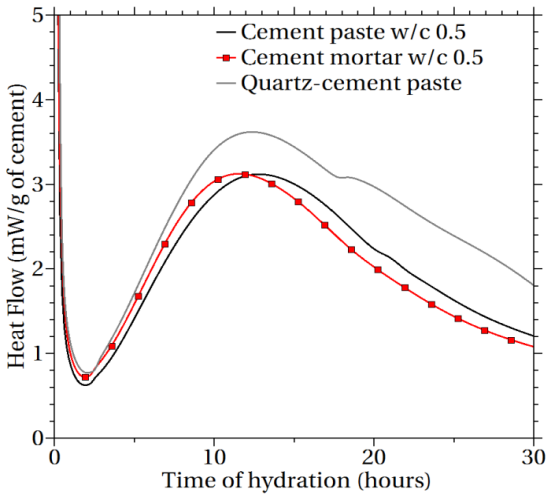
Slag

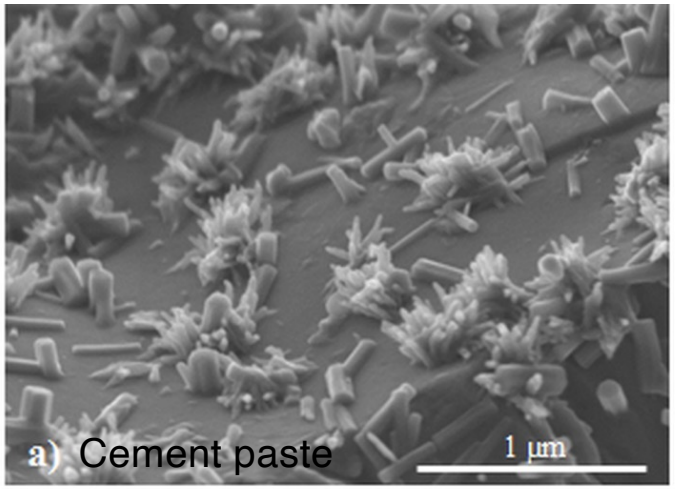


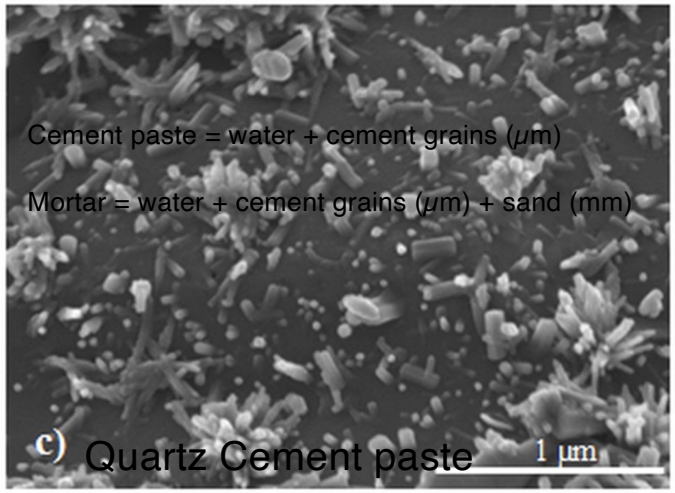
Quartz

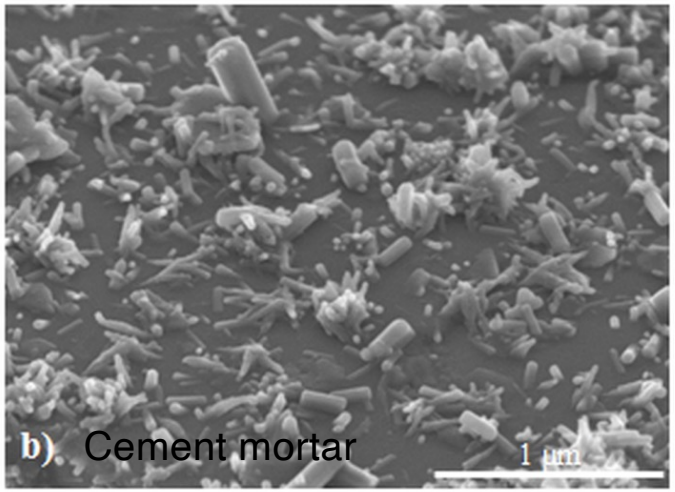
Mortar vs Paste

Berodier et al.



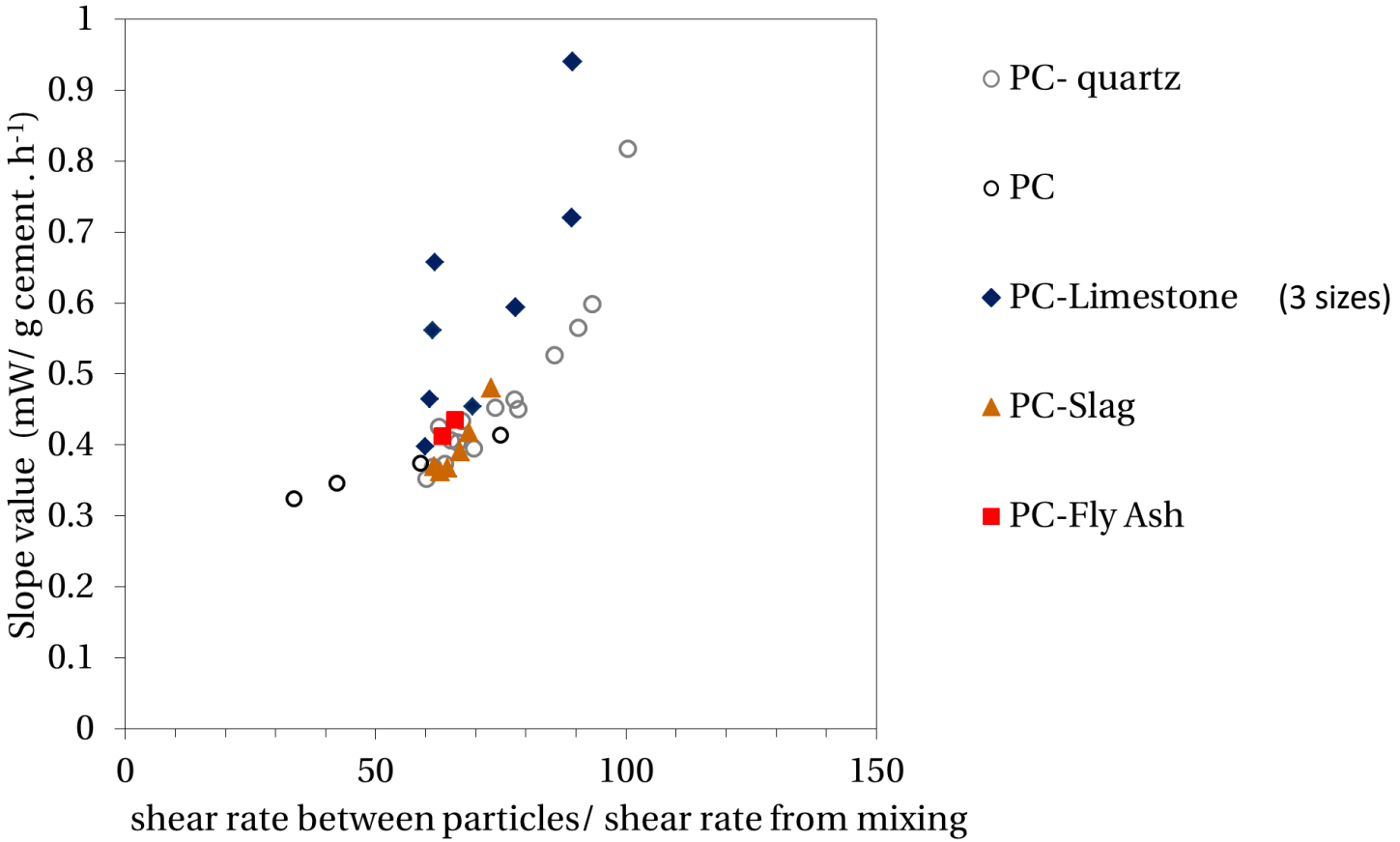






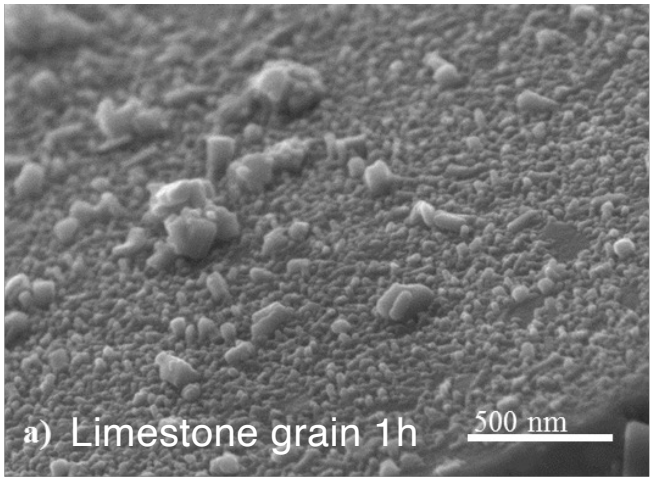
Effect of Slag, Fly ash, Limestone

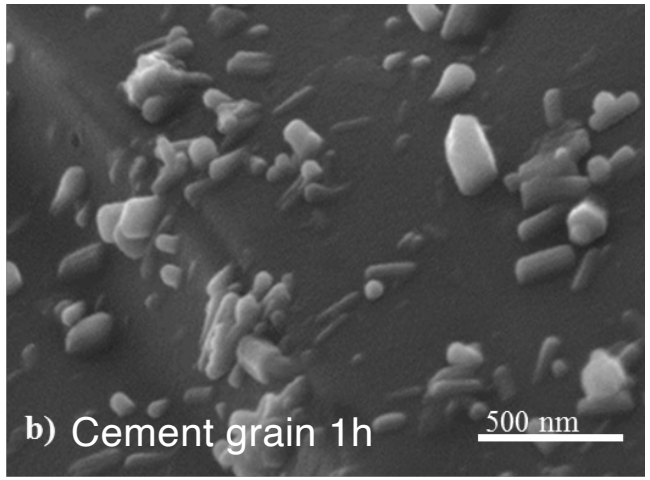
Berodier et al.

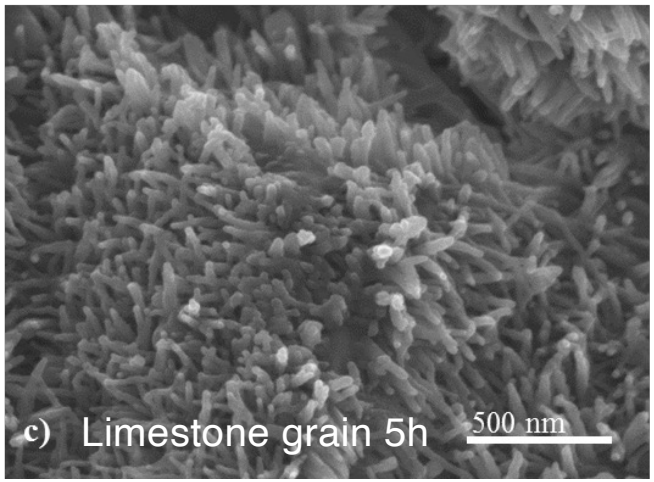


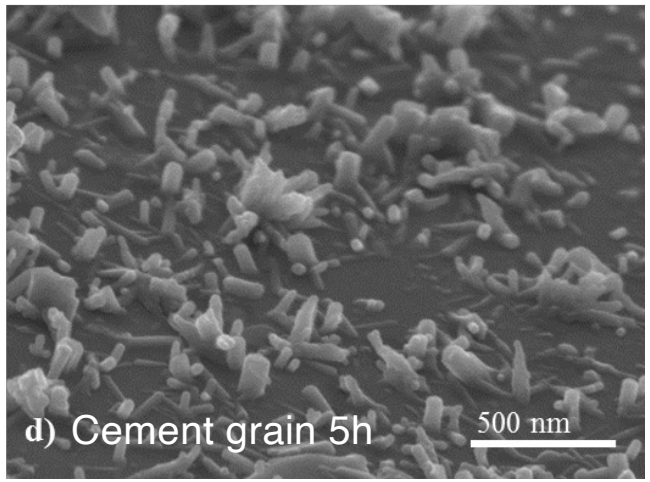
Berodier et al.

Micrographs: Cement + 40% Limestone

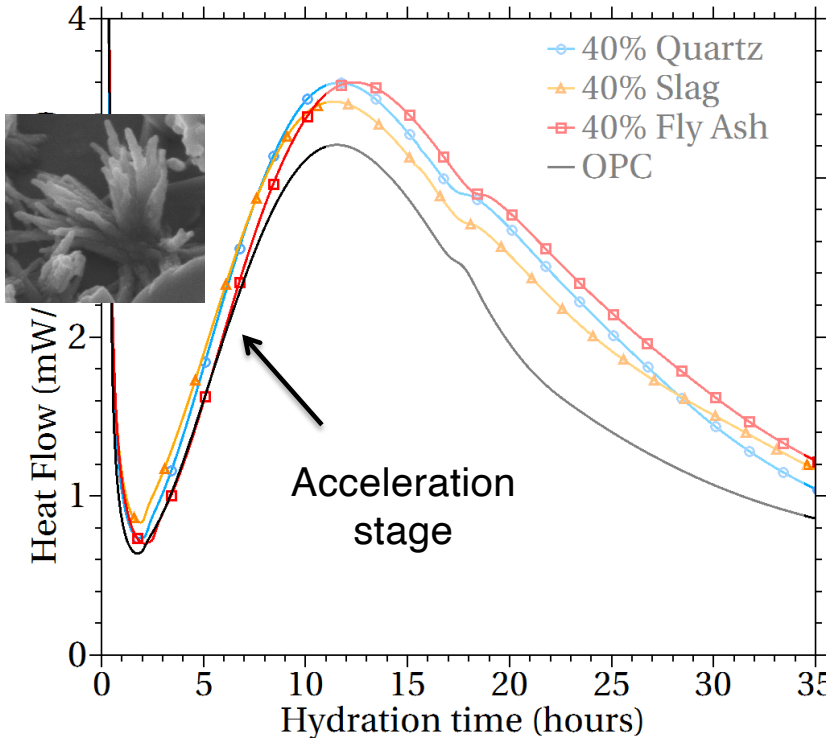








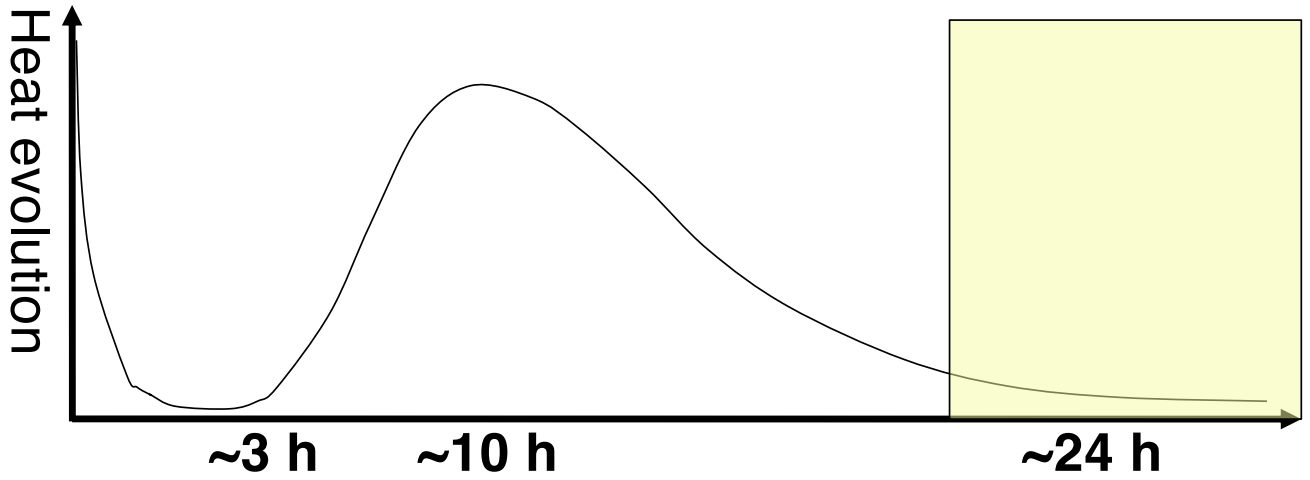
Short summary



Although inert, SCM have a significant effect on the nucleation and growth of C-S-H

- Small increase in nucleation sites ***due to the higher shearing conditions***
- Some surfaces, e.g. calcite might favor the nucleation of C-S-H and also change the growth

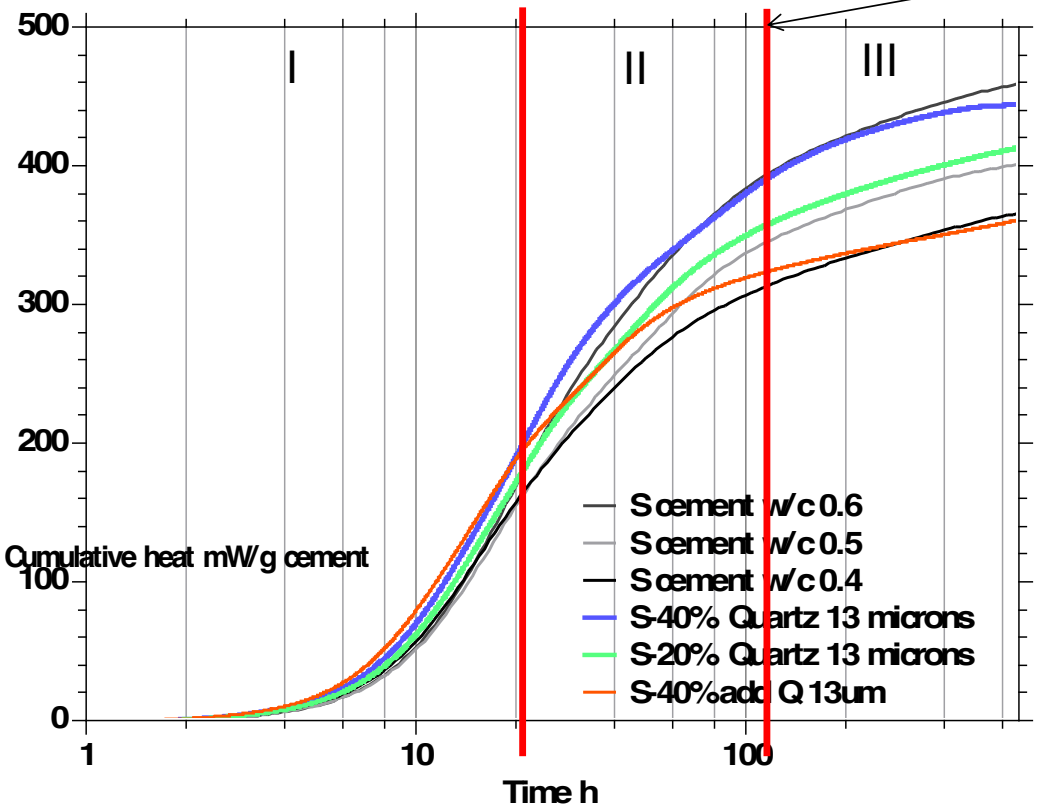
Period III, slow ongoing hydration



- Although this period is most important regarding strength development mechanisms operating have not been studied in detail.

1 or 2 regimes?

About 6 days for w/c = 0.4



II. Space controlled

III. “densification” similar for all systems

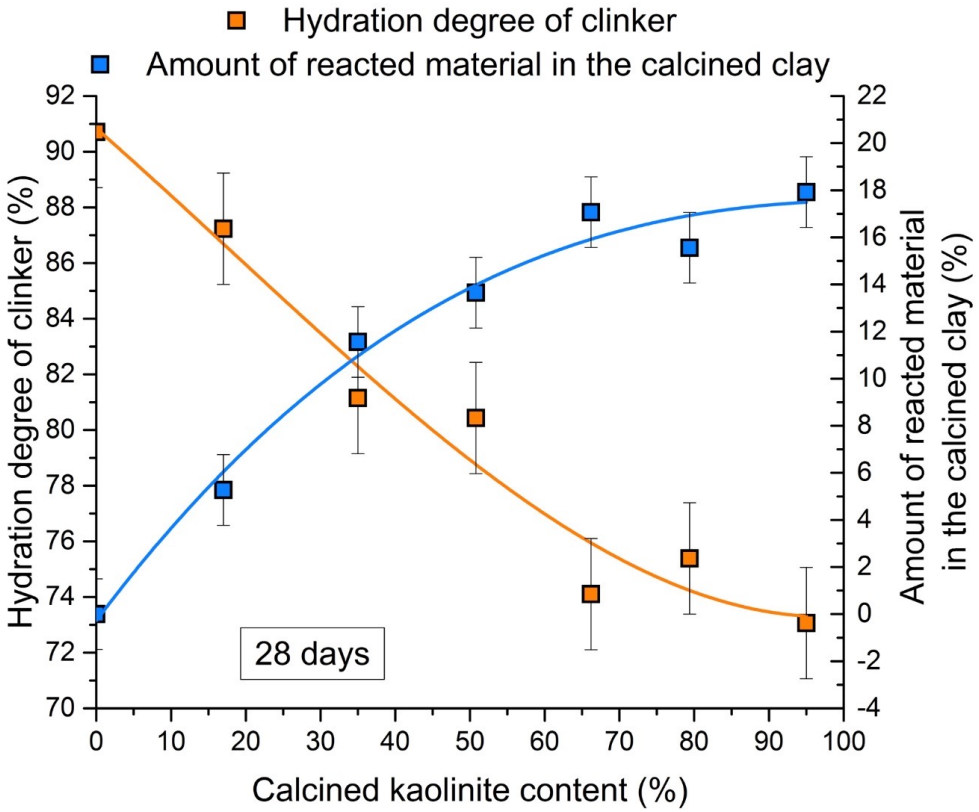
E.Berodier

Space filling

- In first week or so space filling becomes the dominant mechanism
- “competition” between clinker and SCMs
- Hydration clinker $\approx$ calcined clay $\geq$ slag $>>$ flyash

Competition with calcined clay

$$AS_2 + C\overline{C} + CH + H \rightarrow C_4A\overline{C}_{0.5}H_{12} + C - A - S - H$$



- Increase of the grade of calcined clay:
- Global increase of the amount of reacted material in the calcined clay
- Decrease of clinker hydration degree

Questions

- Quelle phase contribue le plus au développement de résistance du béton de ciment de Portland?
- Quels sont les produits principaux d'hydratation de cette phase?
- Le gypse est ajouté pendant le meulage du ciment pour contrôler l'hydratation de quelle phase?
- Quels sont les produits d’hydratation les plus importants résultant de l'hydratation de la phase C3A?