EPFL

Lecture 3: Hydration Kinetics - silicates

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng

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Kinetics are key

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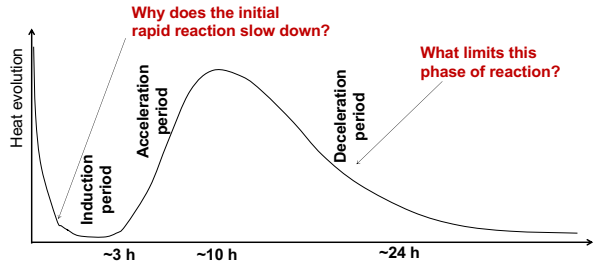
underlying mechanisms not well understood



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- Tremendous progress over last 2 decades
- This work is not in the text books yet
- Some has only just been submitted for publication

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Three periods

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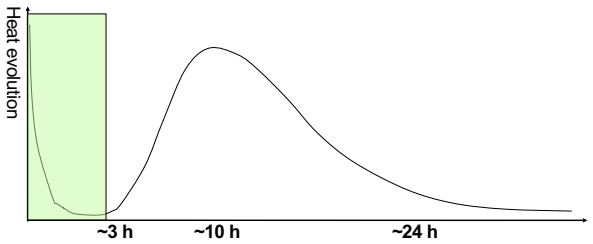
Induction period



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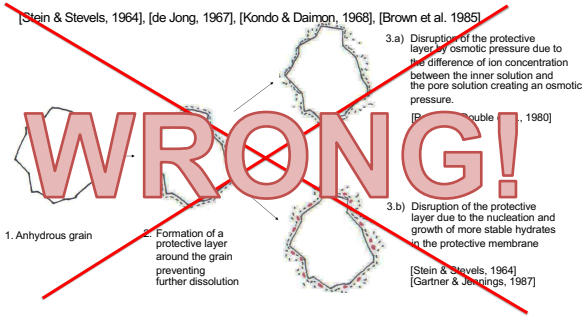
Most wide spread idea

A) PROTECTIVE MEMBRANE LAYER

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



No direct evidence

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Portland cement observed in the cryo SEM

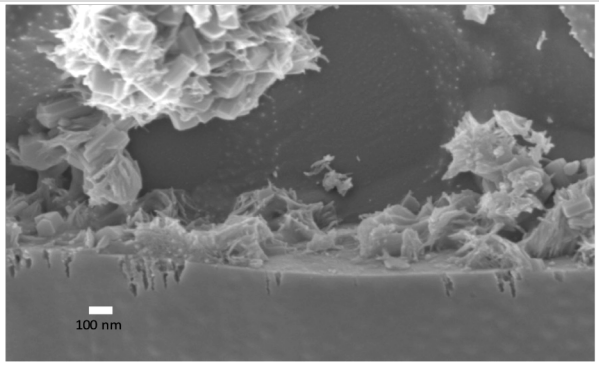

Image from Luc Nicoleau

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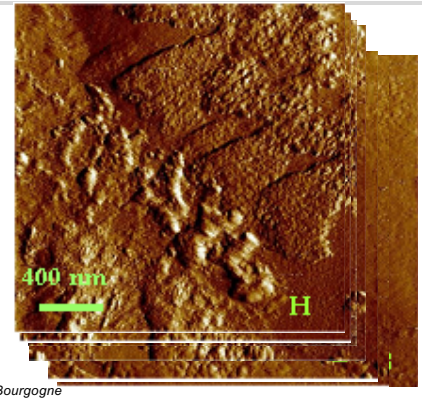
AFM wet cell



Thesis Helène di Murro U. Bourgogne

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Effect of annealing

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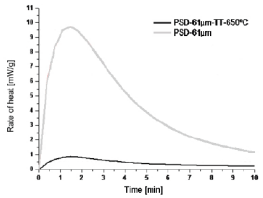
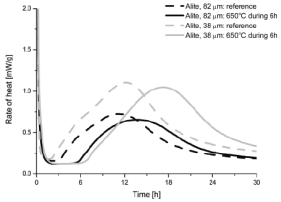
alite of narrow particle size distribution

First dissolution peak



Main hydration peak



This cannot be explained by protective layer theory

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Dissolution = negative growth

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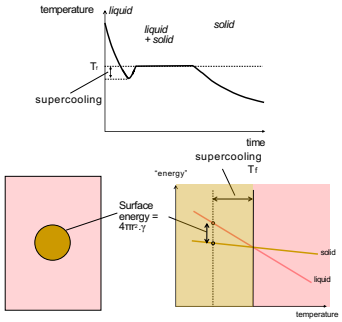
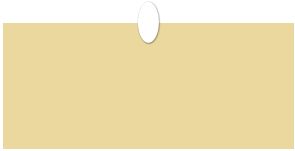


Growth: example solidification of metals
Supercooling due to need to form surface of nuclei

Dissolution from smooth surface also requires energy for extra surface



This energy comes from the undersaturation of the solution

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Study of theories of dissolution from Geochemistry

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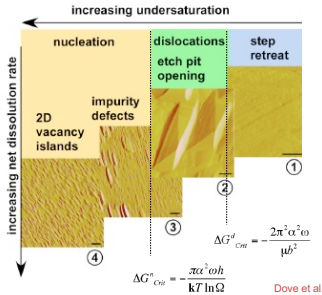
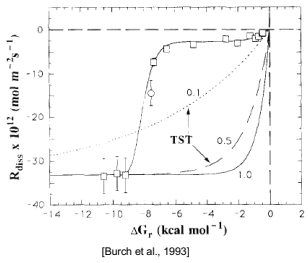
dissolution as negative growth



Dove et al., 2007

Albite dissolution at 80° C and pH 8.8



[Burch et al., 1993]

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Does this apply to alite?

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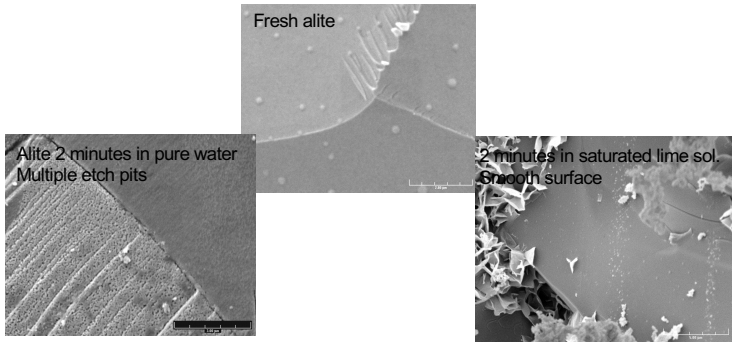

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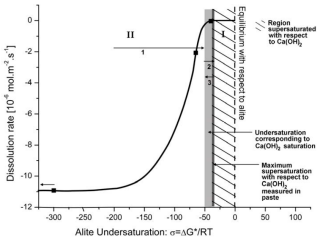
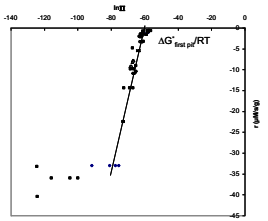
Evolution of the rate of dissolution



Juilland et al 2009
From theory



Nicoleau et al 2011
From experiment

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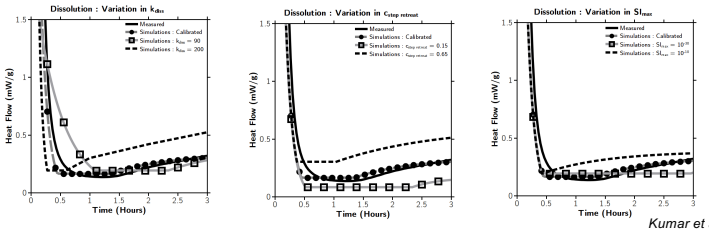
Rate of Dissolution: modelling

- Rate = $k_{diss} \cdot a_{SSA} (SI_{max} - SI_{alite}) + a_{SSA} \cdot c_{step\_retreat}$

SI_{alite} = IAP/K_{sp} of alite
SI_{max} = Critical undersaturation of alite
a_{SSA} = Specific surface area

- k_{diss}, SI_{max} and $c_{step\_retreat}$ are calibrated from model systems

Fast dissolution regime
Step-retreat regime



Kumar et al 2012

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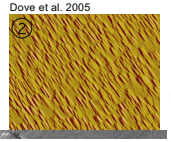
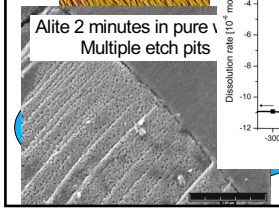
Theories of dissolution from Geochemistry

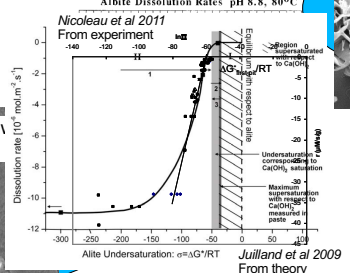
dissolution as negative growth

Dove et al. 2005



Alite 2 minutes in pure v
Multiple etch pits

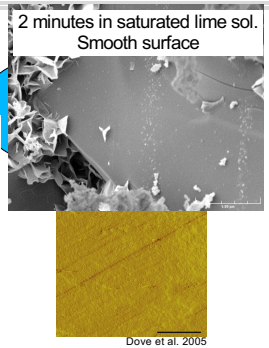




Nicoleau et al 2011
From experiment

Juilland et al 2009
From theory

2 minutes in saturated lime sol.
Smooth surface



Dove et al. 2005

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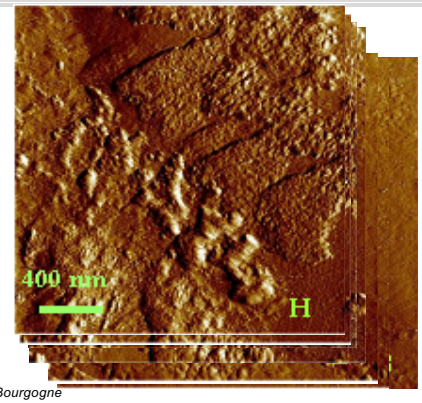
AFM wet cell



Thesis Helène di Murro U. Bourgogne

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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 fit to calorimetry curves;
  - Can explain all experimental observations.

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the Main Hydration Peak

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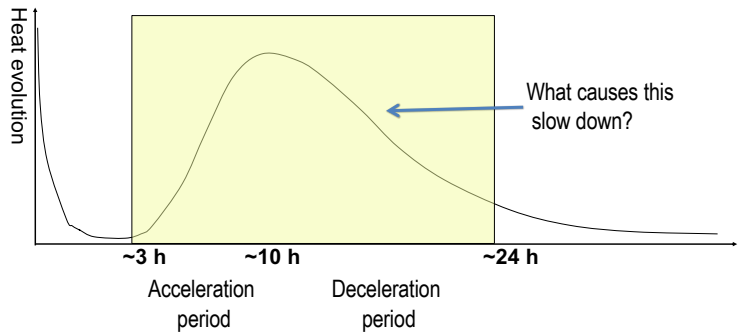
Period II, main heat evolution peak



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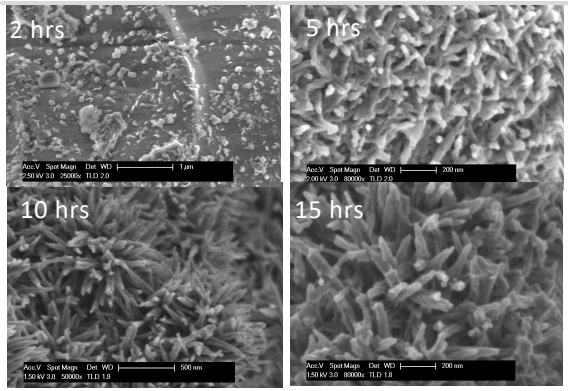
End of induction period growth of C-S-H (& CH)



Berodier 2015

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Beware of fitting!

- At least 5 different mechanisms have been fitted to the data set of Costoya!
- They cannot all be right!
- Scherer, Zhang & Thomas (2012) – analytical modelling of boundary nucleation and growth
- Bishnoi & Scrivener (2009) - densifying C-S-H growth
- Masero, Thomas & Jennings (2013) - limited zone for hydrates
- Honorio, Bary, Benboudjema & Poyet (2016) - confined zone
- Ouzia and Scrivener (2019) - rapid growth of C-S-H to critical length

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Main hypotheses for slow down

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

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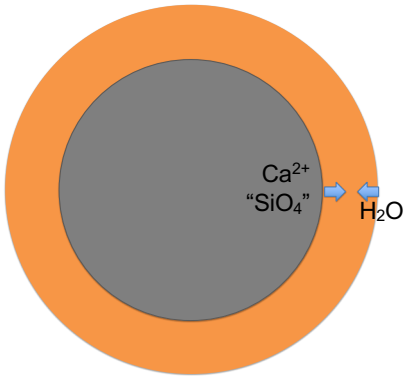
Diffusion



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

Rate limiting step is the diffusion of species through this layer

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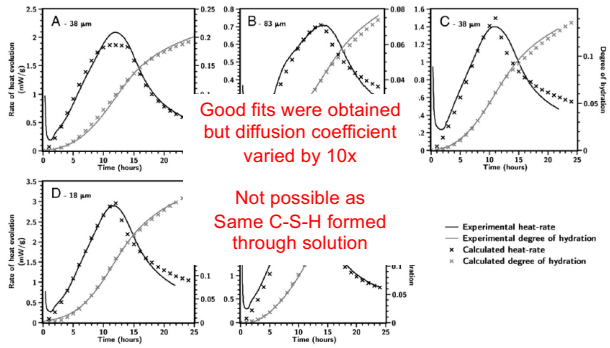
Bishnoi 2008 : Post-peak "Diffusion"



Good fits were obtained but diffusion coefficient varied by 10x

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

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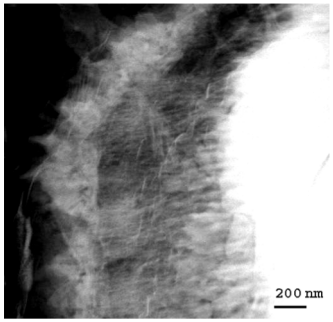
Evidence against diffusion

- 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

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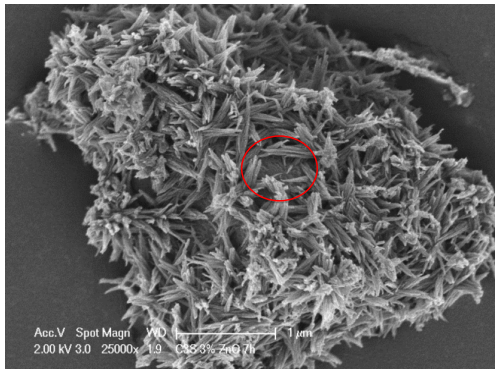
The "layer" is incomplete



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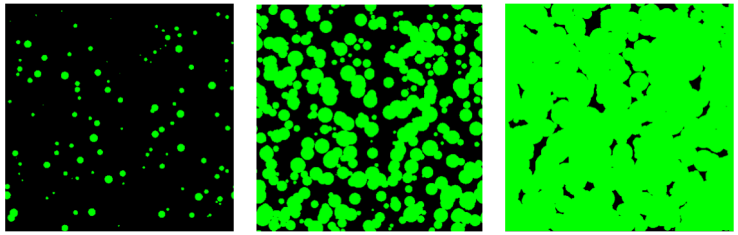
Impingement: Avrami



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

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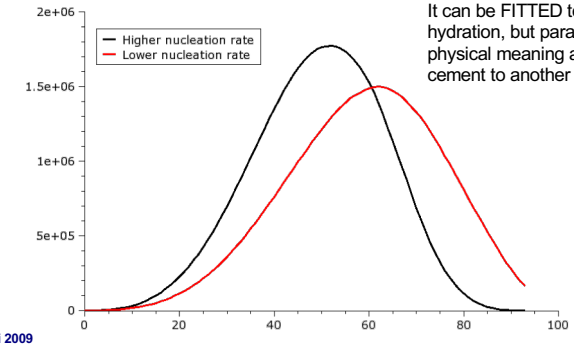
Avrami equation gives the right kind of peak



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

Bishnoi 2009

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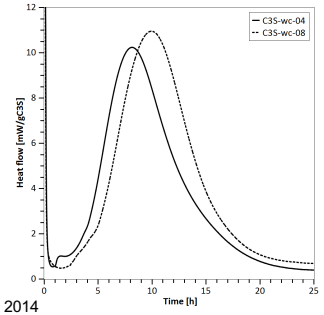
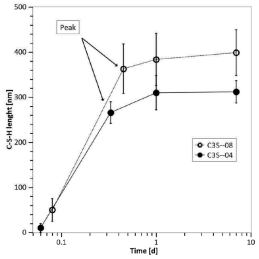
Impact of w/c

- 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

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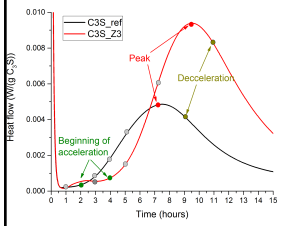
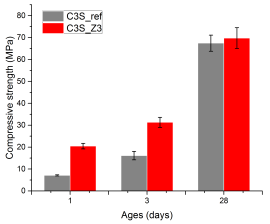
Impact of zinc





Micro mortar (2x2x2cm³) compressive strength

Li 2020

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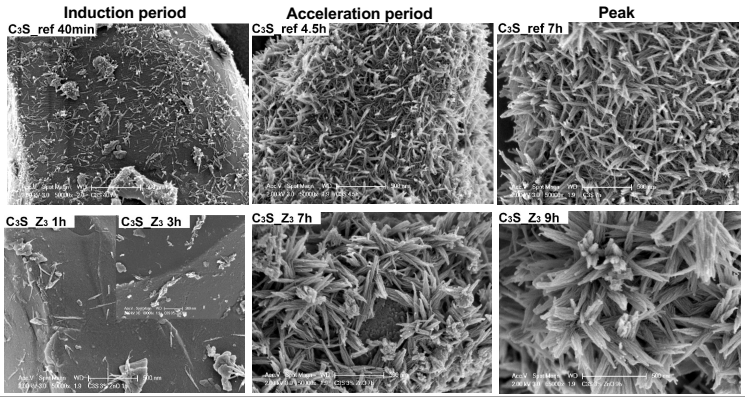

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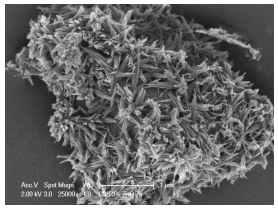
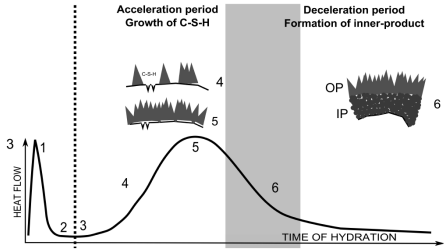
Bazzoni's scenario





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

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Needle model: Ouzia 2017

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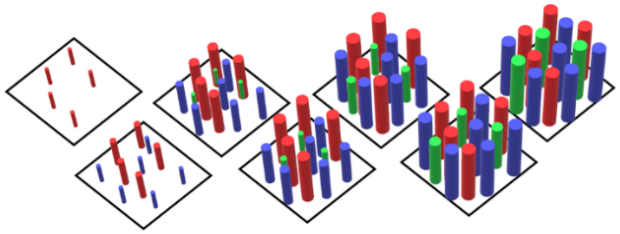
- C-S-H growth as needles
- ALL parameters from experiment – **NO fitting**



Ouzia, A., Scrivener, K.
The needle model: A new model for the main hydration peak of alite
Cement and Concrete Research, 115, January 2019, Pages 339-360

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Needle model: Ouzia 2017

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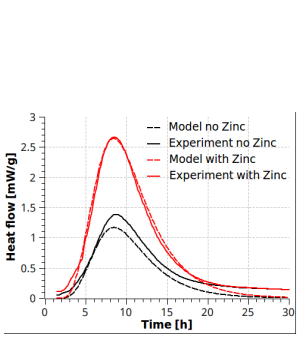

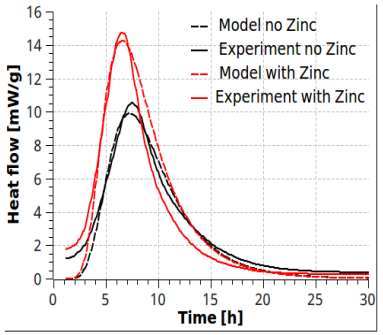

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Open question?

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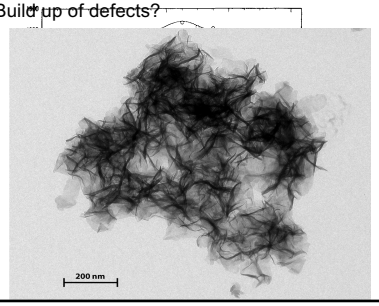
- If mechanism is C-S-H growth: What controls this?

  Solution composition ?

  Build up of defects?



Other?

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Main peak, summary

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- Many hypotheses can fit the form of the peak
- Need to look at
  a wide range of variables and have physically measureable parameters
- Growth of needles to a critical length seems best hypothesis

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after the main peak

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Period III, slow ongoing hydration

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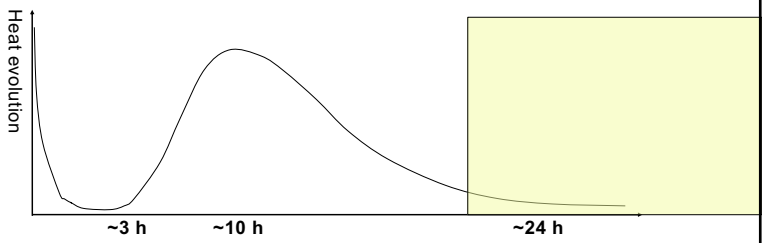

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Practical importance of long term

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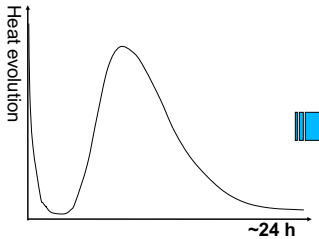

28 days

~ 50% reaction
~ 25% strength

~ 80% (+30) reaction
~ 80% (+65) strength

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Cumulative heat curves: 2 regimes after main peak

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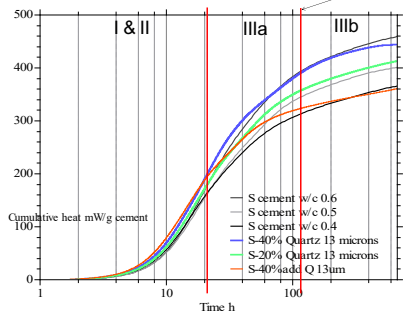
About 6 days for w/c = 0.4



Hydration of systems with different w/c or amounts of filler

IIIa. Space controlled

IIIb. "densification" similar for all systems

E.Berodier

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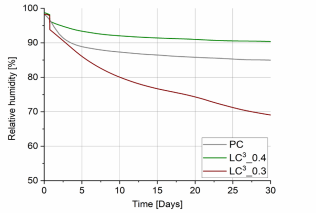
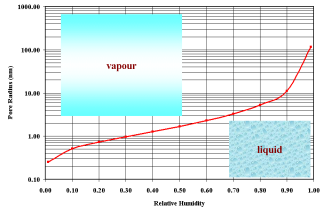
Limitations to hydrate growth

- Hydrates mainly grow in solution filled pores
- In sealed systems:
  - Voids form ($V_{hydrates} < V_{anhydrous} + V_{water}$)
  - Relative humidity reduces
  - Only pores below a certain size contain solution

99% ~100nm
95% ~50 nm
85% < 10 nm





Kelvin-Laplace equation

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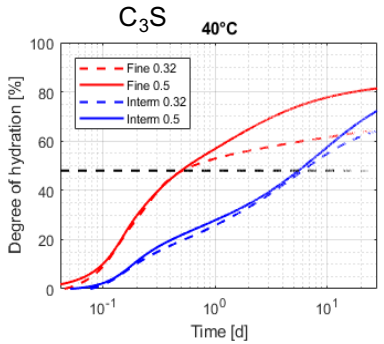
Rule of thumb for lack of solution filled pores

$$DoH_{SF} \approx 1.5 * w/c$$

After this point dramatic slow down in rate of reaction

These experimental results also prove that diffusion is not the limitation:

0.5 mix have higher reaction rate at a higher degree of hydration



Ouzia, PhD thesis 2018 and submitted

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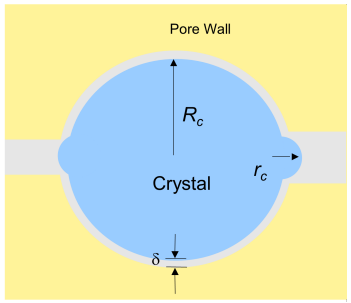
Growth into smaller pores slows down



Adapted from R. Flatt

- Growth of hydrates into small pores requires increased curvature
- Increased curvature means higher activity of ions in solution in equilibrium
- Therefore higher activities needed to keep growing

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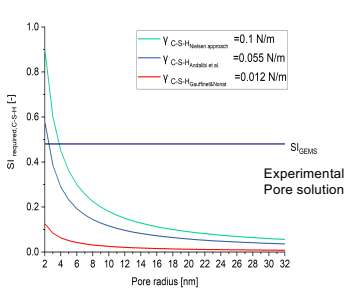
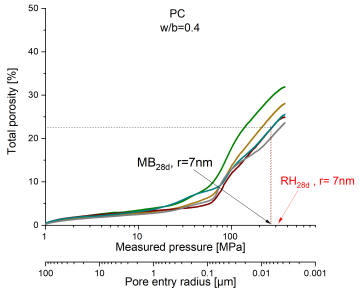


C-S-H growth

Briki et al 2021



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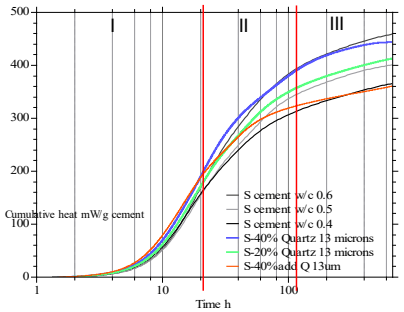
Long term



In stage III Kinetics still do not fit with diffusion

E.Berodier

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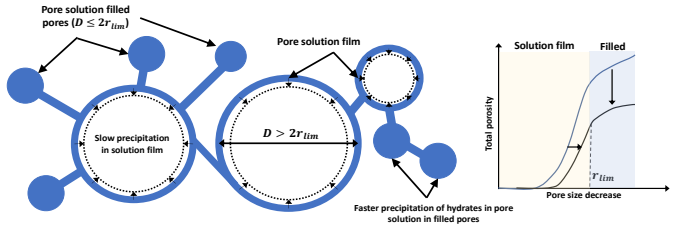
Over long term there appear to be 2 types of hydrate growth

- Changes from 90 days to 3 years



Zunino et al submitted 2021

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Summary: long term

- In the longer term rate of reaction limited by size of solution filed pores
- Upper limit, decease in maximum size of solution filled pores at relative humidity decreases
- Lower limit, increasing “curvature” of crystals, requires higher activity in solution for growth.
- In long term hydrate grow, increasingly slowly in the solution filed pores
- Also seem to have slow growth on surface of larger (mainly vapour filled) pores, .

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Dominant mechanisms

- Up to the end of the induction period:
  - Dissolution rate of C_3S
- Main heat evolution peak
  - Rapid Growth of C-S-H “needles” to certain length
- Longer term
  - Lack of solution filled pores

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