

Using micromechanics and poromechanics to explore Delayed Ettringite Formation

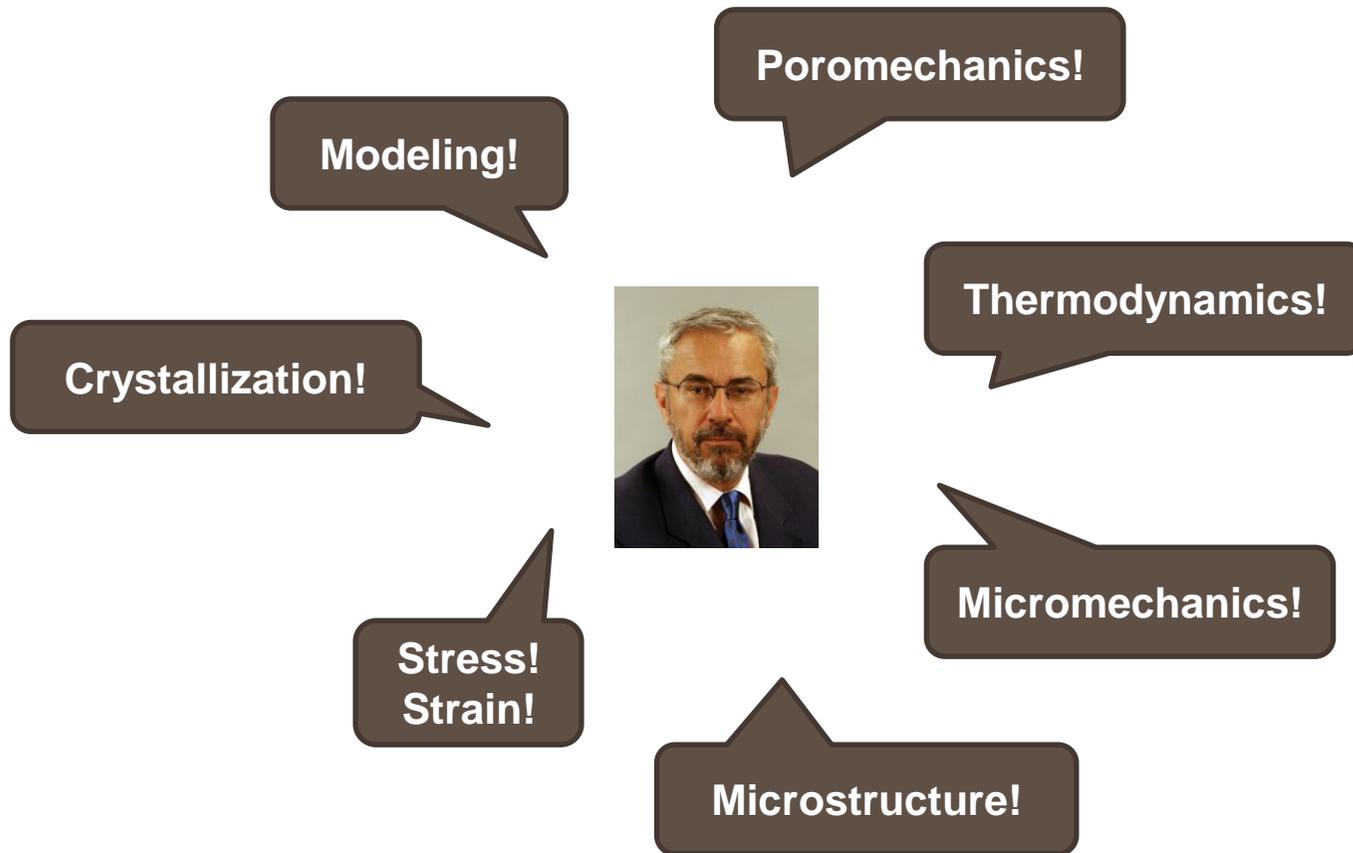
Rémi Barbarulo

From Concrete Nanoscale to Structure:
Celebrating Gilles Chanvillard's memory
July 2016



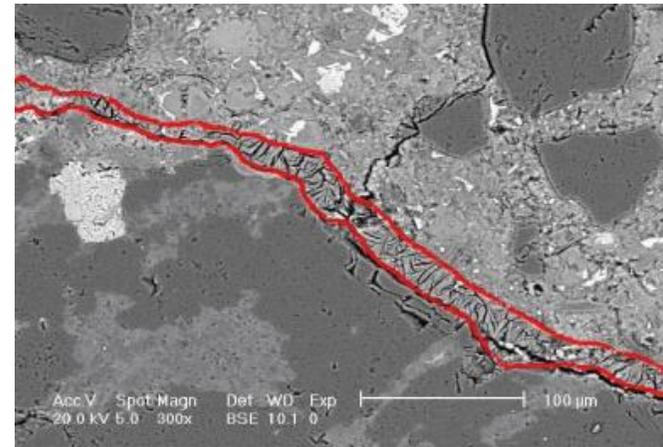
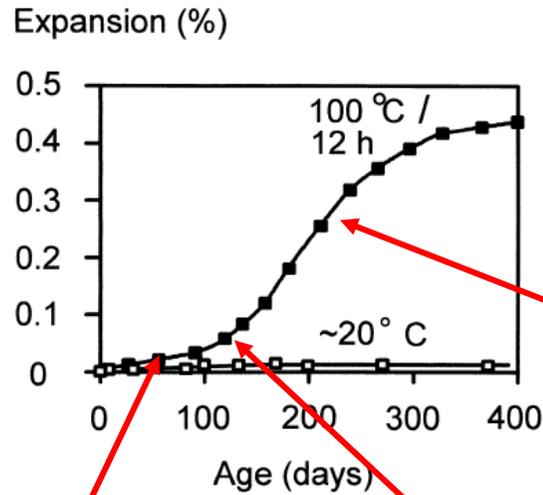
The day Gilles put pressure on me...

Mechanics and Physics of Porous Solids (MPPS) - A tribute to Prof. Olivier Coussy



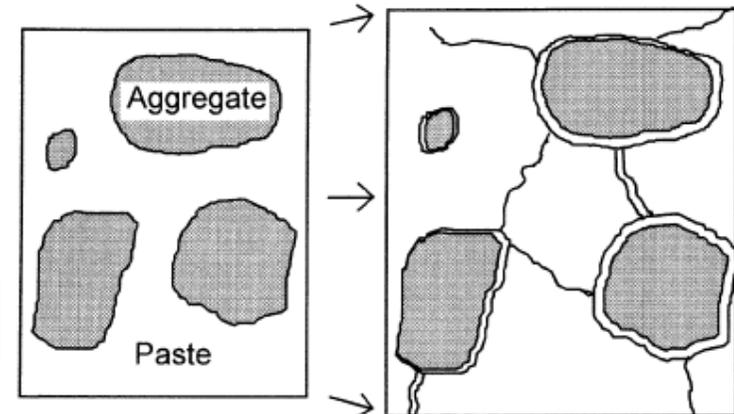
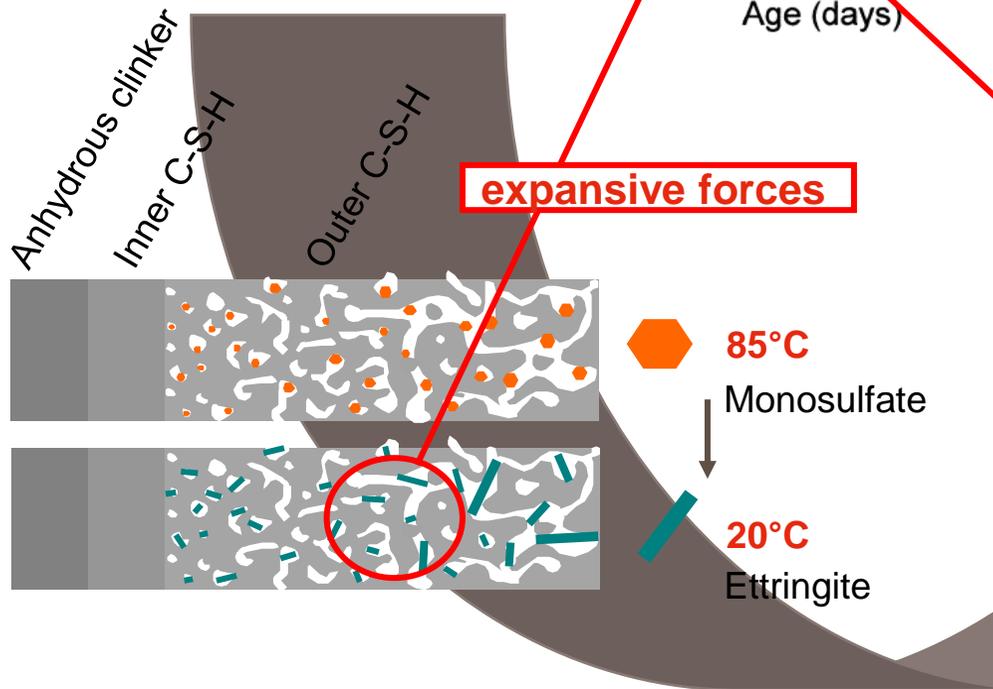
Delayed Ettringite Formation

Initial state :
ettringite precipitates in outer C-S-H

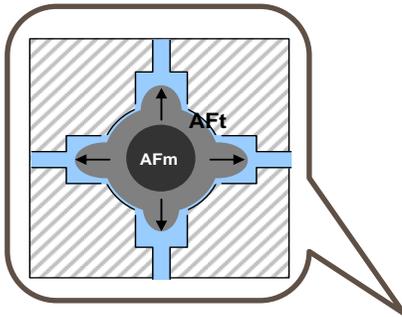


Final state : Ostwald ripening localizes ettringite in large space

Threshold stage : uniform paste expansion creates damage and gaps around aggregates



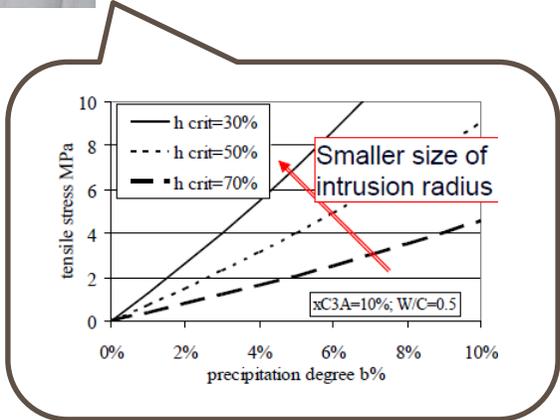
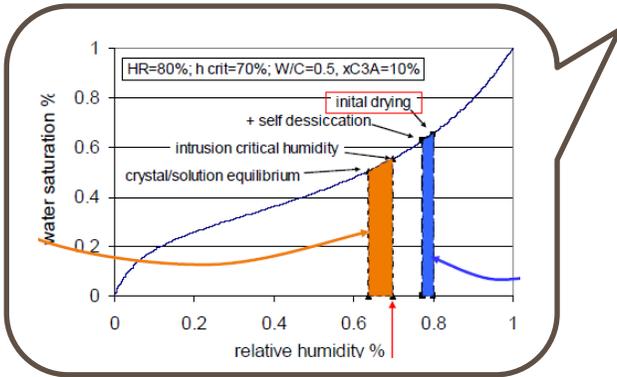
The day Gilles put pressure on me...



$$W = \frac{1}{2} \left[\frac{b^2}{K} + \frac{(b - \phi_0)}{k_s} \right] [S_C \cdot \Delta p_C + S_L \cdot \Delta p_L]^2$$

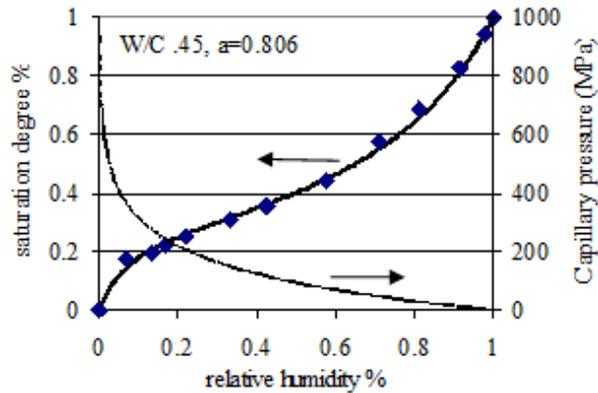


$$K = \frac{4g_s k_s (1 - \phi_0)}{3\phi_0 k_s + 4g_s}$$

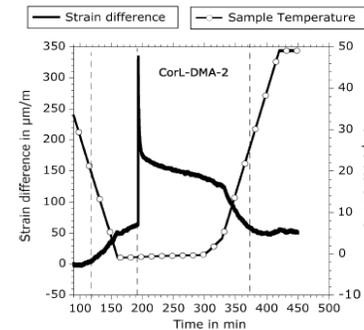


A framework and some questions

Microstructure and shrinkage

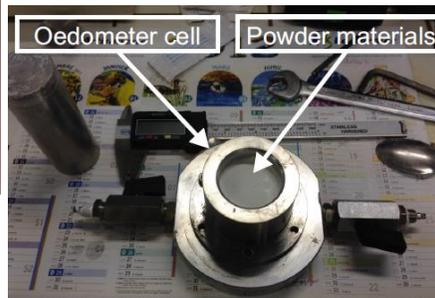


Transient strains induced by crystallization?

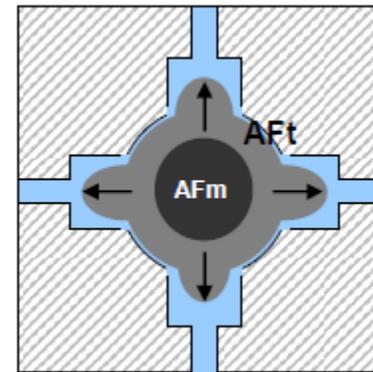


(Espinosa-Scherer, 2008)

Stresses induced by crystallization at equilibrium



Delayed Ettringite Formation

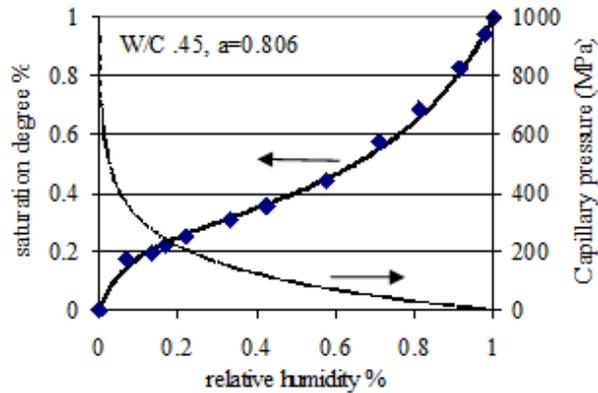




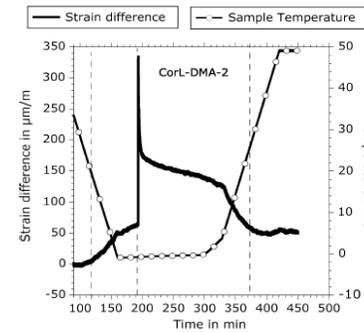
A few steps with Gilles Understanding (?) sulfate attack in concrete

A framework and some questions

Microstructure and shrinkage

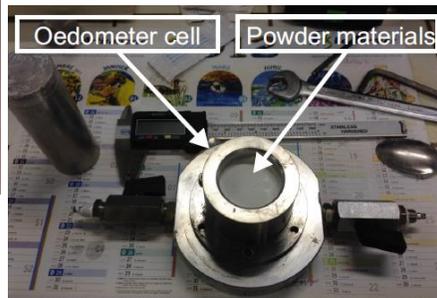


Transient strains induced by crystallization?

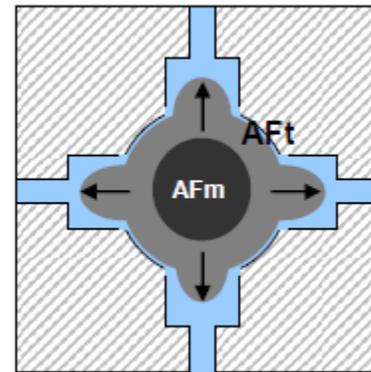


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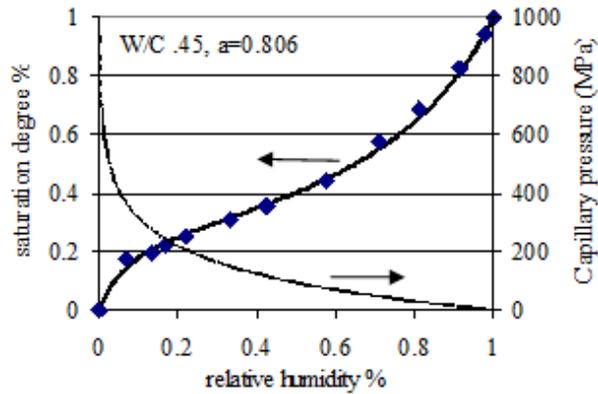


Delayed Ettringite Formation

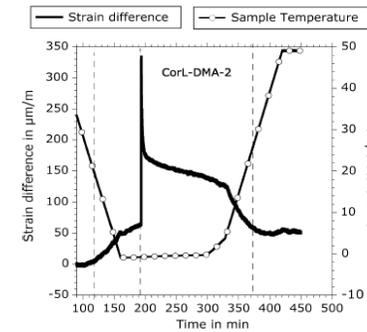


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Microstructure and shrinkage

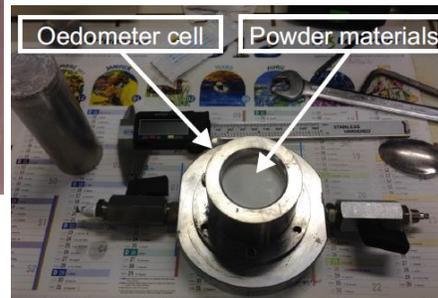


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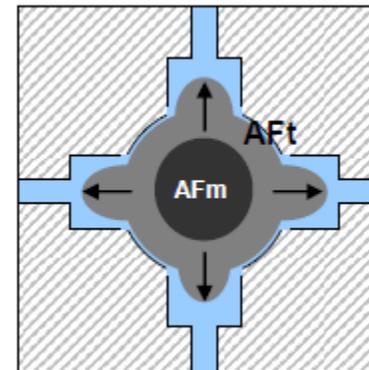


(Espinosa-Scherer, 2008)

Measuring stresses induced by crystallization



Delayed Ettringite Formation



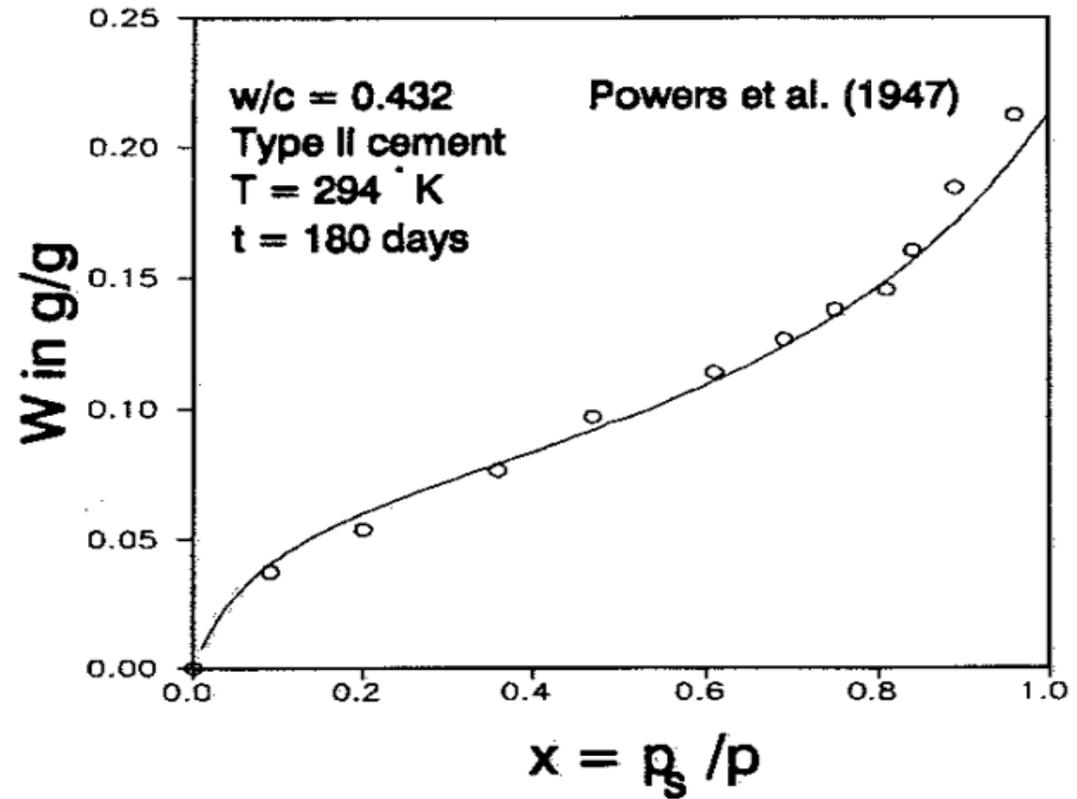
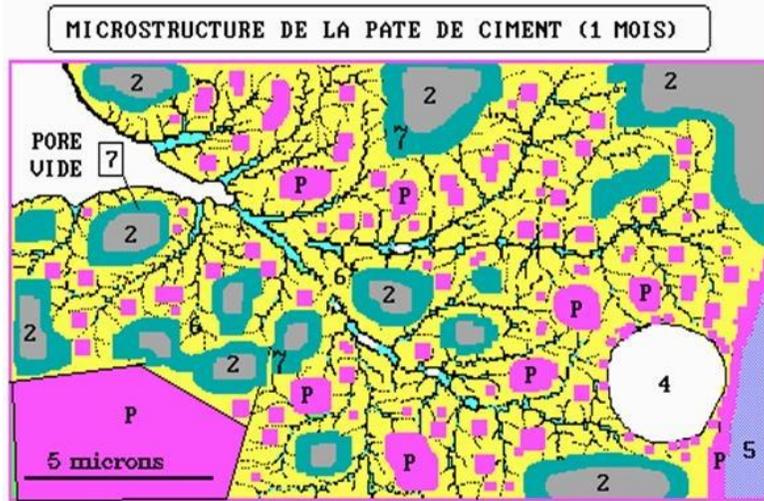
Simulation de la Microstructure et des Retraits des mélanges Réactifs en cours de Solidification (SiMiRéSol) – 2000

“ […]

As a conclusion, we believe this study is original in the sense that we are pioneers in such an approach, starting from the microstructure so as to predict a macroscopic behavior, such as shrinkage.

Since the 30's, **E. Freyssinet** and after **T. C. Powers** had anticipated this modeling approach, and the main factors influencing shrinkage. But it is only with the development of the mechanics of partially saturated porous materials (generalizing the concept of effective pressure in soils, introduced by **Biot** in the 50's, and which was rigorously formalized only 10 years ago by **O. Coussy**) that such a modeling was made possible.

Water desorption isotherm, another way to express the porosity

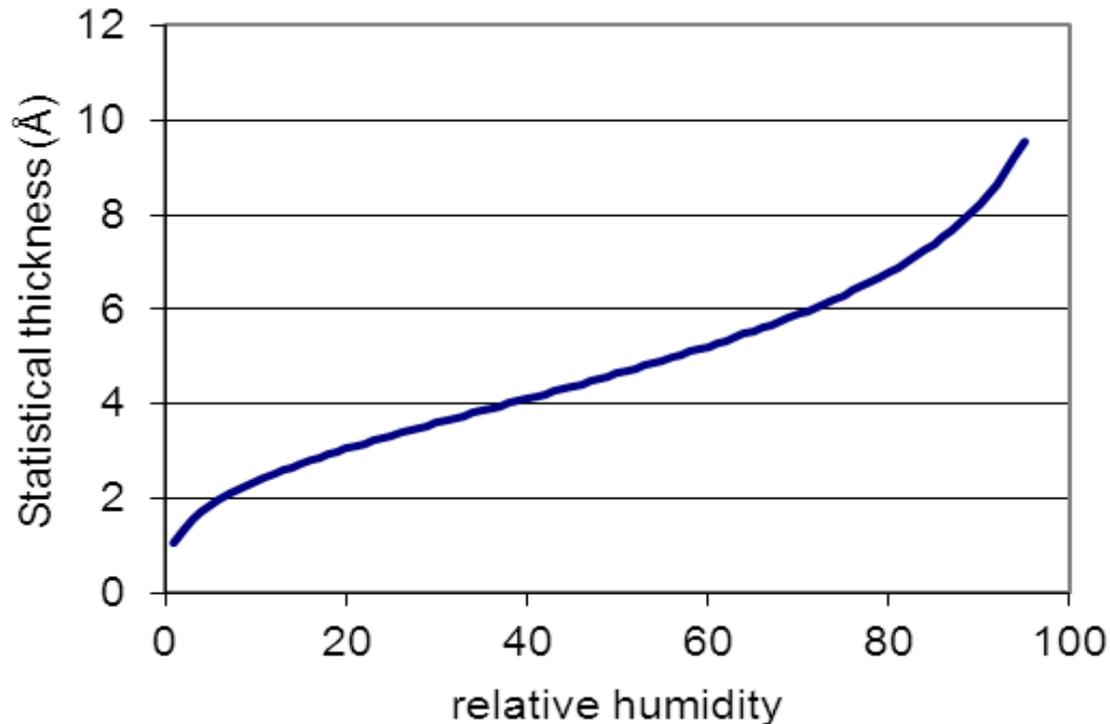


For a given relative humidity:

- water is adsorbed on solid surface
- and fills pores below a fixed pore size

Water Isotherm: building on t-plot

Thickness of the adsorbed water film (t-plot) on calcium silicate surface



R. Badmann & co.,
JCIS, 1981

- **C-S-H is the most abundant phase in hardened cement paste, specific surface ~ 350 m²/g**
- **Water adsorption isotherm can be modelled based on t-plot**

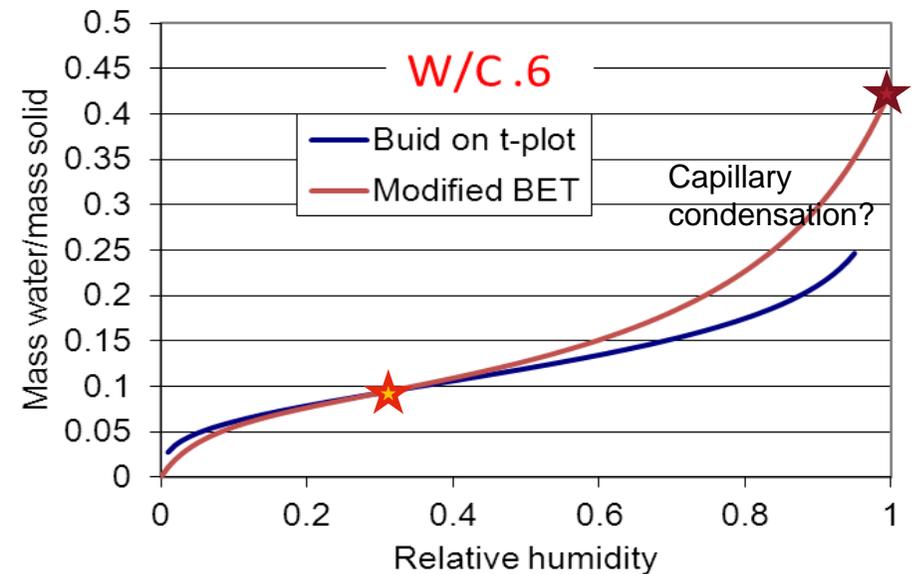
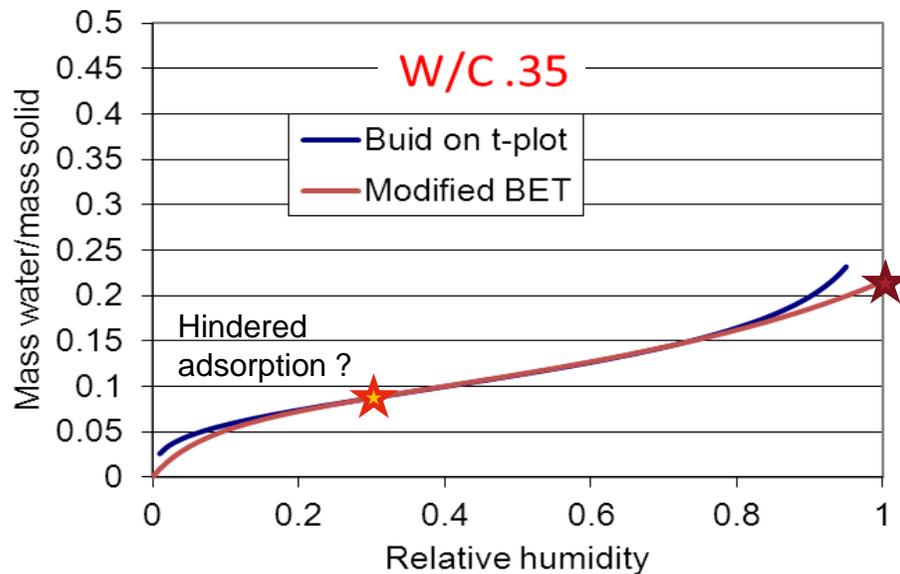
Water Isotherm: building on t-plot vs modified BET

Modified BET equation to describe the adsorption isotherm:

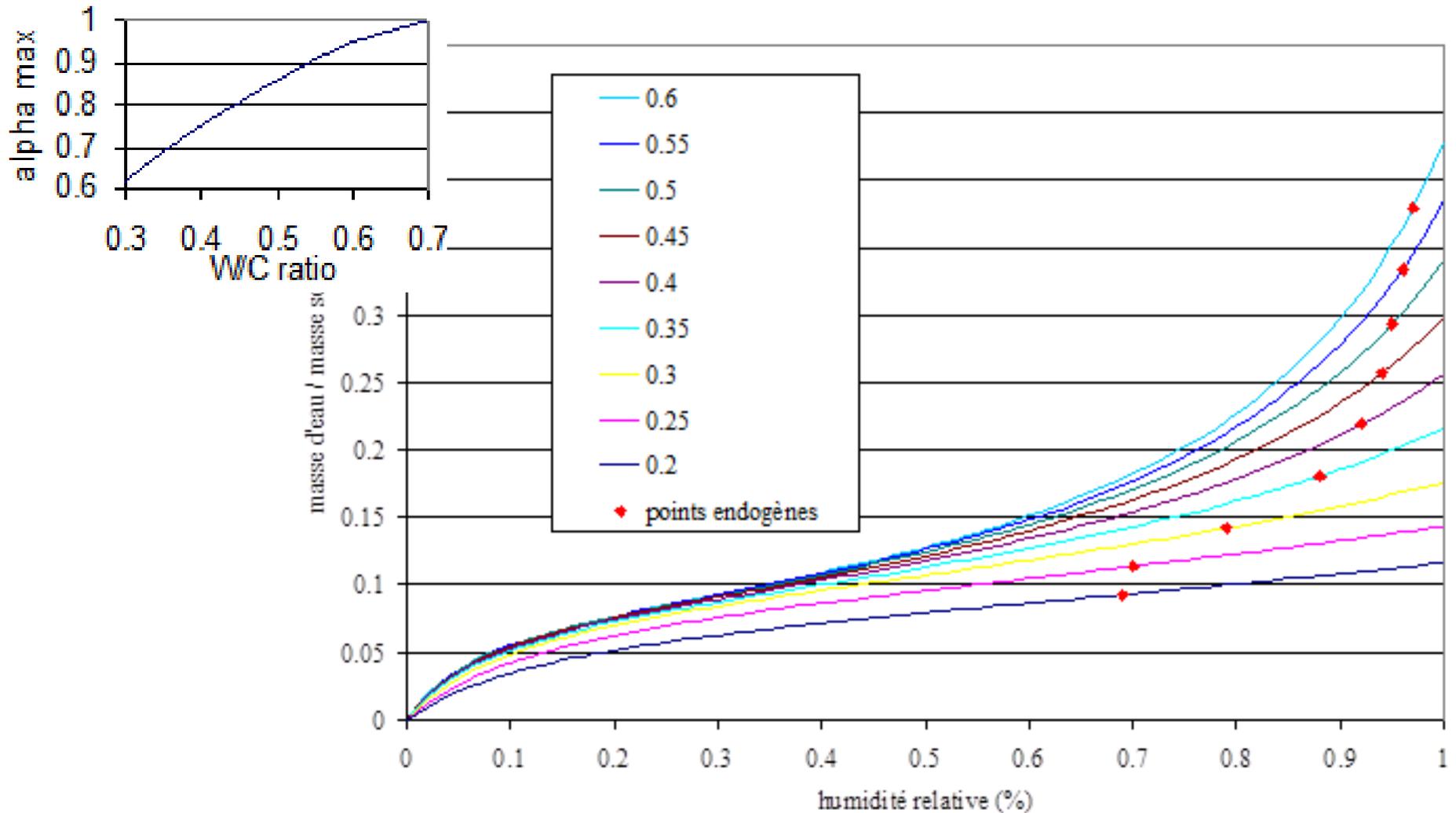
$$W = \frac{C.k.V_m.h}{(1-k.h)(1+(C-1).k.h)}$$

Y. Xi & co., ACBM, 1994

- It is commonly assumed that at 30%, no capillary pores remain => t-plot point ★
- Considering mass / volume balance of hydration, total porosity ★ can be estimated
- Adsorption heat “C” being known, k and Vm can be estimated

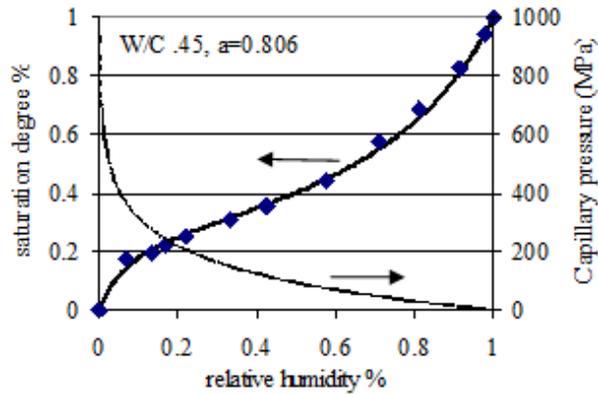


From mix-design to water absorption isotherm

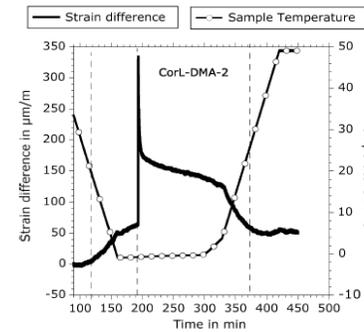


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Microstructure and shrinkage

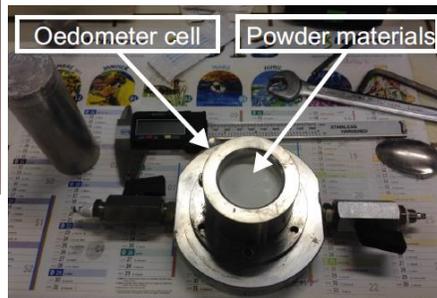


Transient strains induced by crystallization?

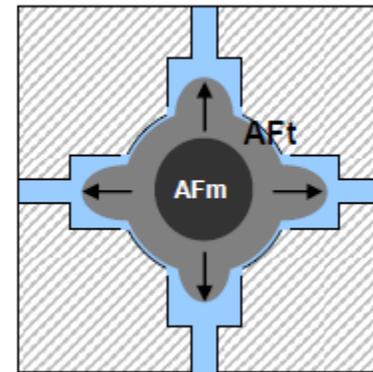


(Espinosa-Scherer, 2008)

Stresses induced by crystallization at equilibrium



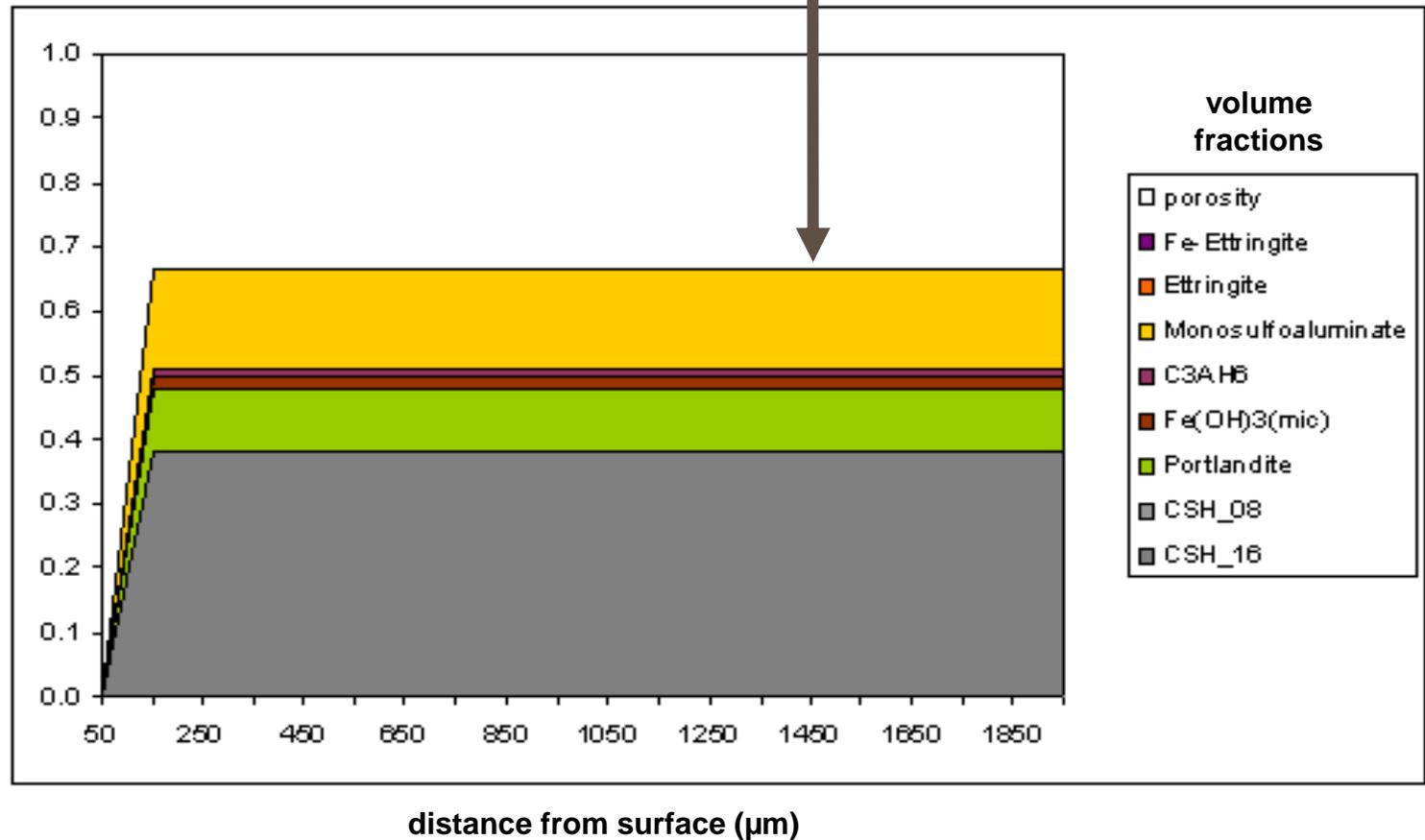
Delayed Ettringite Formation



Transient strains induced by crystallization?

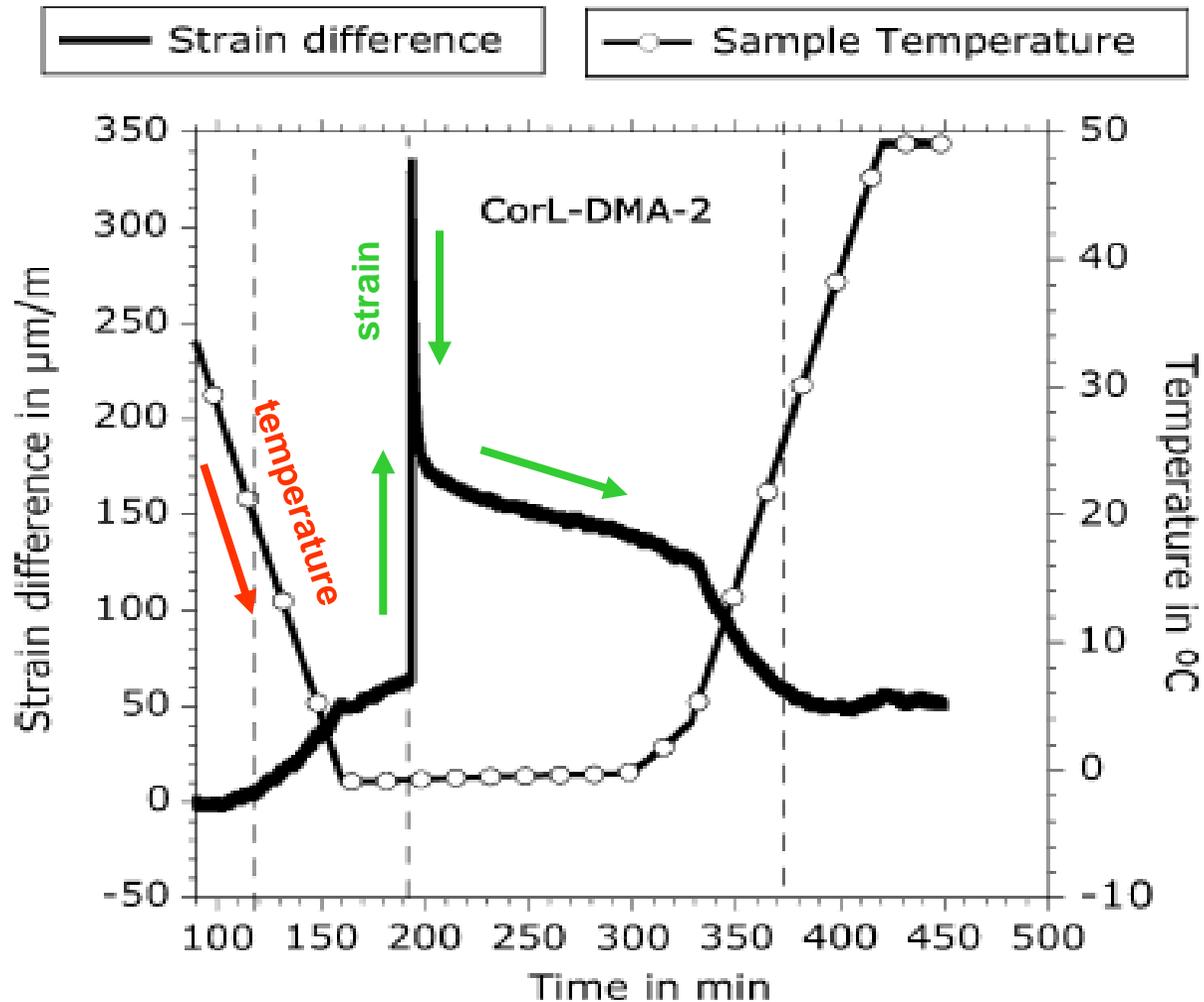
The deeper into the sample, the slower the ionic supply → closer to chemical equilibrium, no supersaturation possible?

15 mmol/L
Na₂SO₄

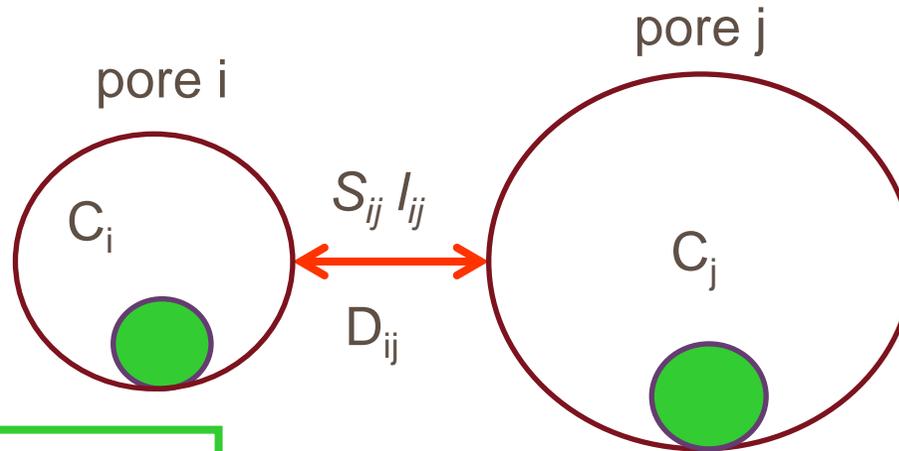


Local equilibrium?

Sodium sulfate precipitation in stones



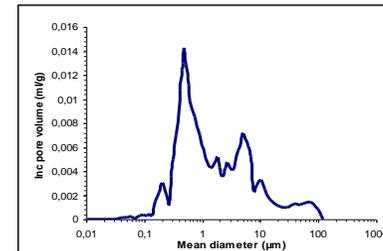
Modeling crystallization and diffusion between pores



$$\frac{dn^x}{dt} = k \cdot A^x \cdot \log(\beta - 1)$$

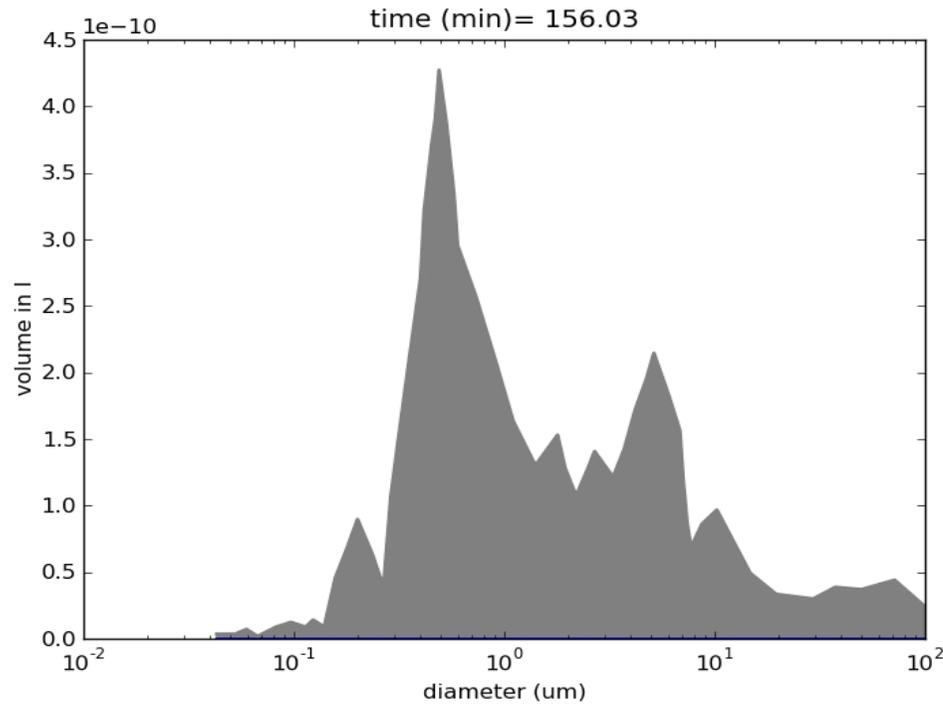
$$\frac{dn^d}{dt} = D_{ij} \cdot S_{ij} \cdot \frac{C_i - C_j}{l_{ij}}$$

- + rules for nucleation
- + integration over the whole pore distribution



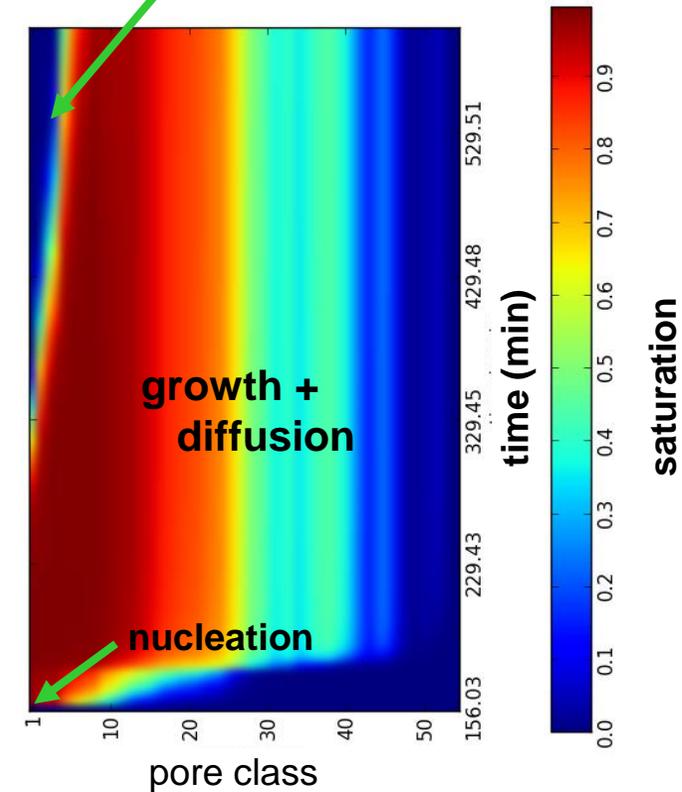
Pore size distribution of Cordova Cream limestone (Espinosa-Scherer 2008)

Application to Cordova cream Limestone

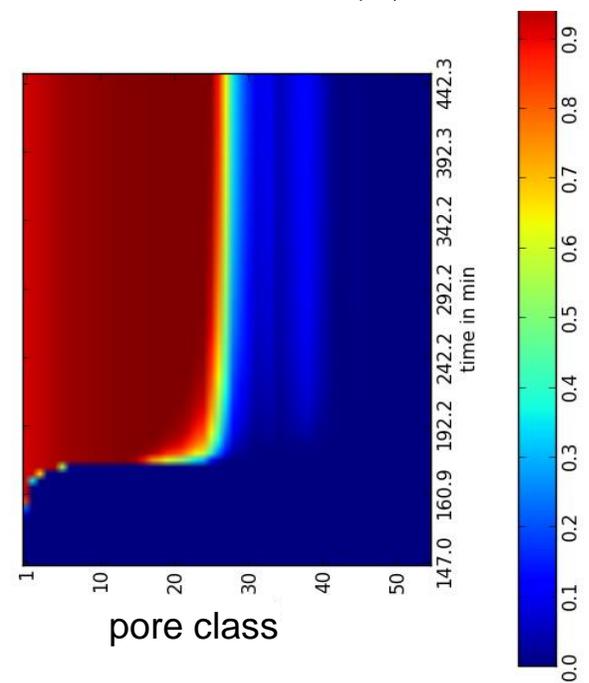
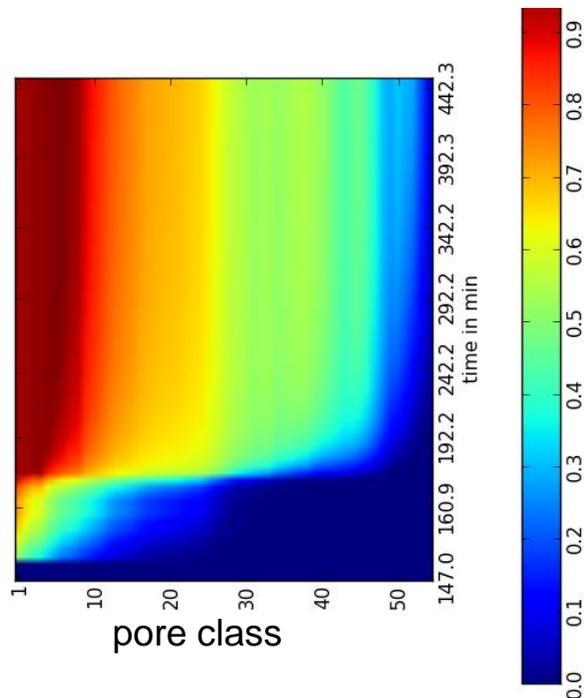
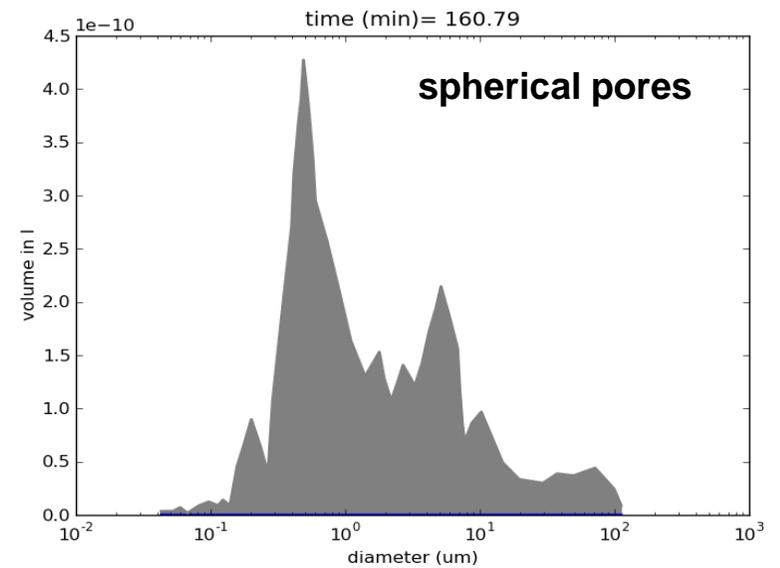
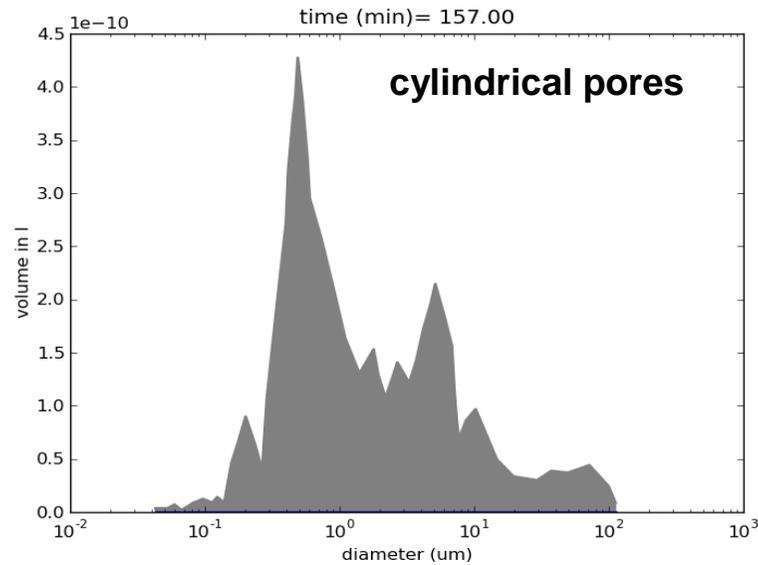


Abdessamad Akkaoui, 2011

dissolution of the smallest crystals (Ostwald ripening)



Impact of pore shape



Abdessamad
Akkaoui, 2011

Generalization of the model

- Crystallization

$$\frac{dN_i^x}{dt} = z_i k A_i^x \left(\frac{K_{eq}}{K_i^*} \beta_i - 1 \right)$$

- Diffusion

$$\frac{dN_i^T}{dt} = D \sum_{j \neq i} n_i n_j S_{ij} \frac{(b_j - b_i)}{l_{ij}} f(s_i^x, s_j^x)$$

- Crystal pressure

$$P_i = \frac{RT}{V_m} \ln \left(\frac{K_{eq}}{K_i^*} \beta_i \right)$$

- Effective pressure

$$P_i^{eff} = f(s_i^x) P_i = s_i^x P_i$$

- Strain

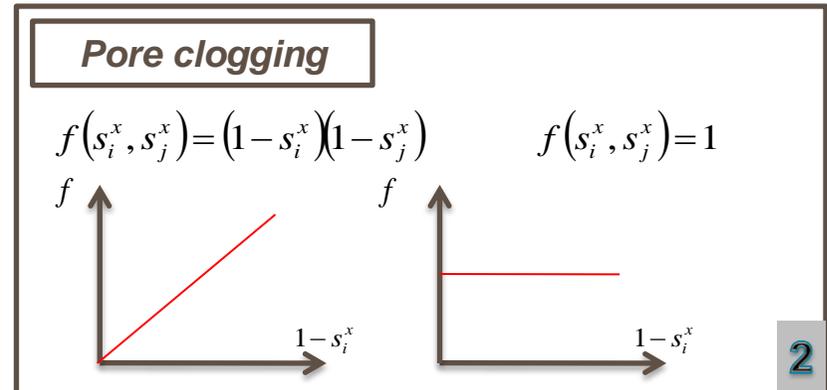
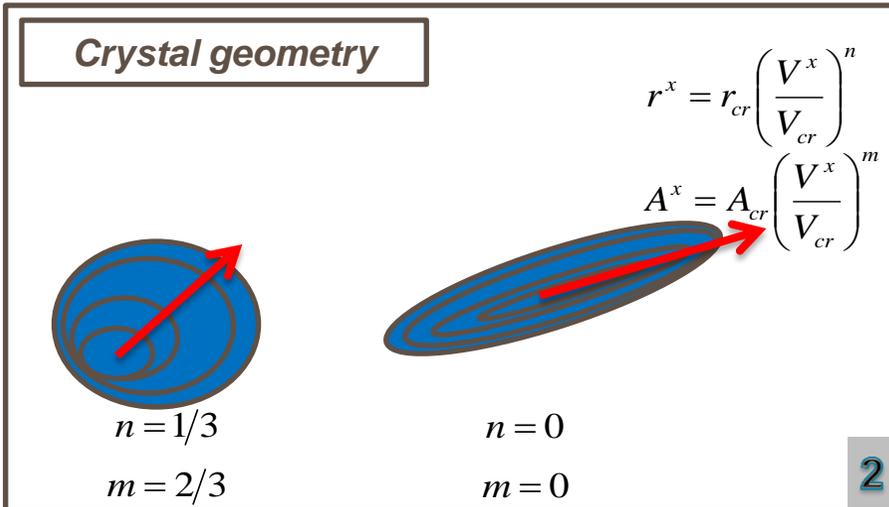
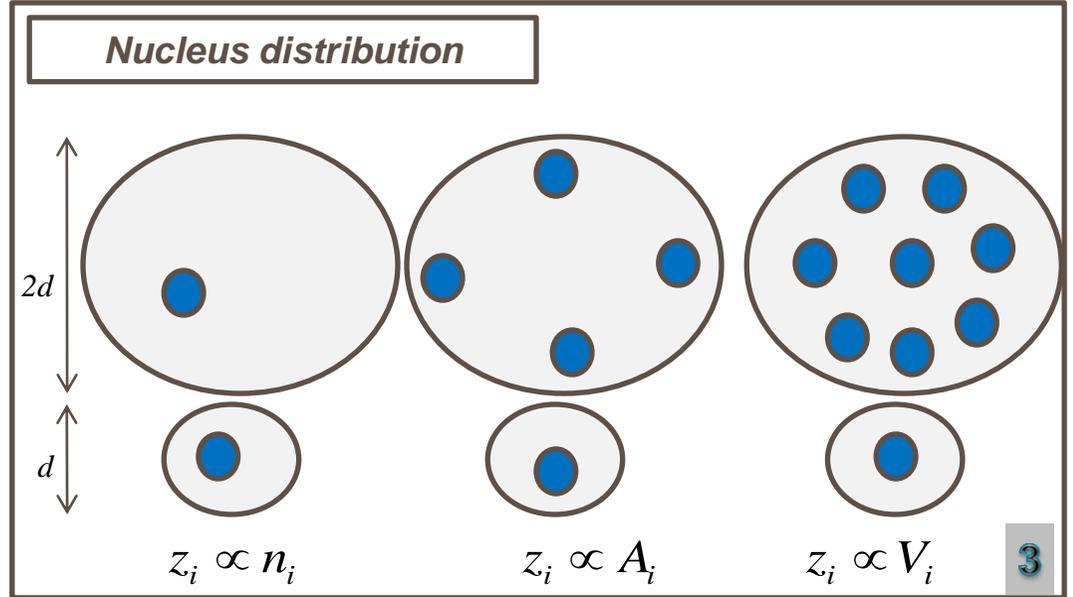
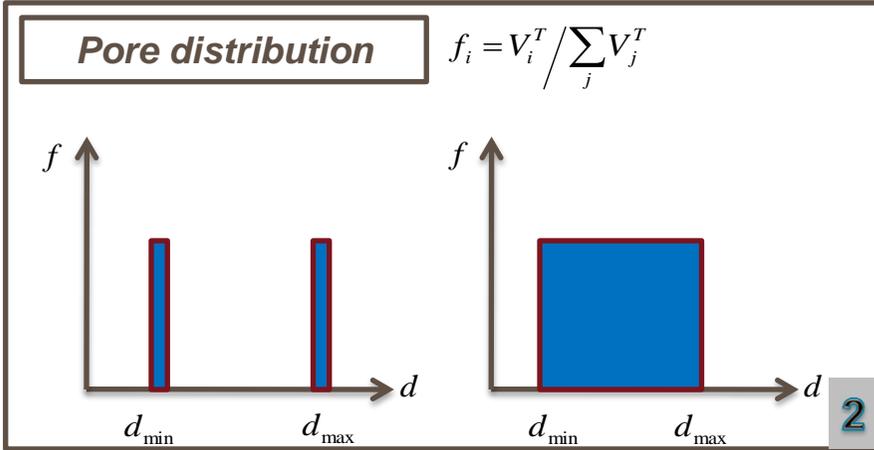
$$\varepsilon = \frac{b}{3K} \sum_i f_i P_i^{eff}$$

Abdusalam Aili, 2012

Poromechanics

$$\begin{cases} \sigma = K\varepsilon - bP \\ \varphi = b\varepsilon + P/N \\ s_{ij} = 2Ge_{ij} \end{cases}$$

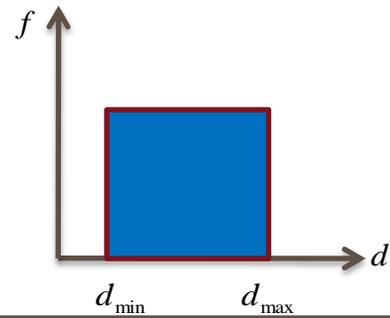
Parametric study



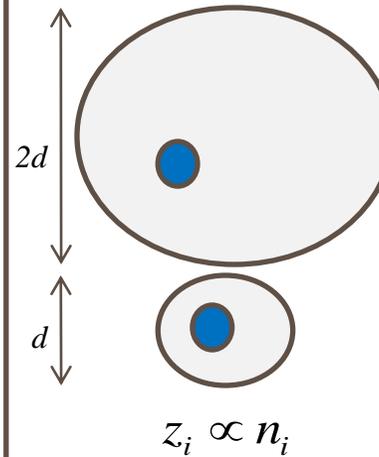
Description of one case

Pore distribution

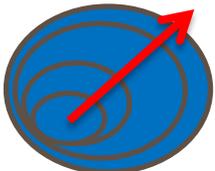
$$f_i = V_i^T / \sum_j V_j^T$$



Nucleus distribution



Crystal geometry

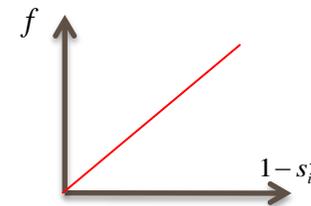


$$n = 1/3$$

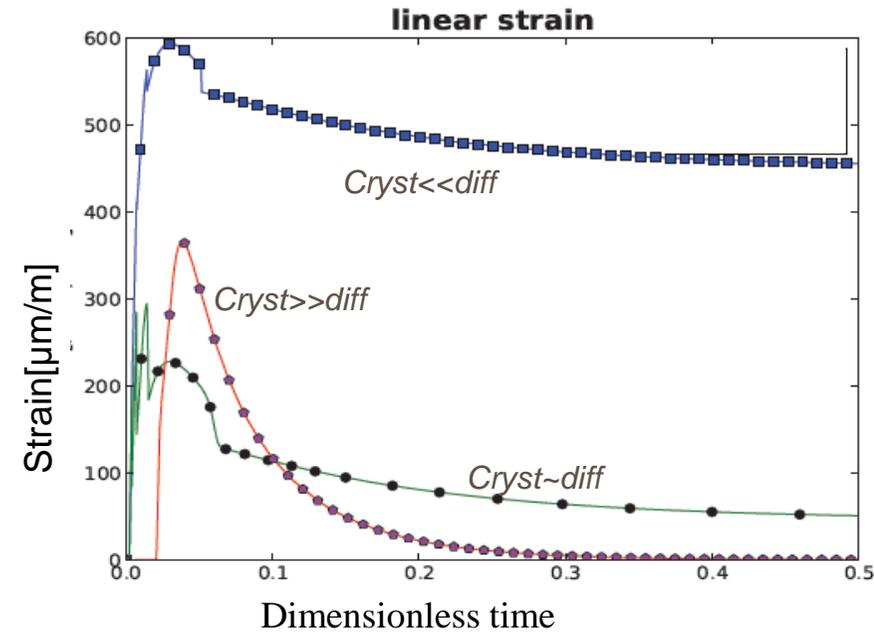
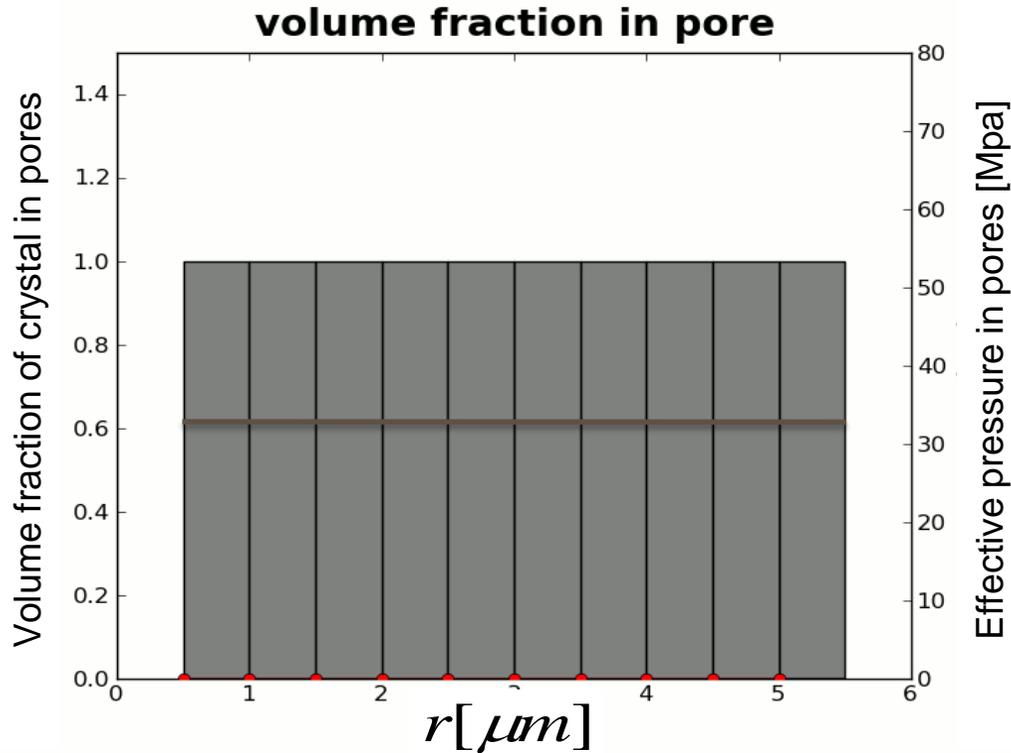
$$m = 2/3$$

Pore clogging

$$f(s_i^x, s_j^x) = (1 - s_i^x)(1 - s_j^x)$$



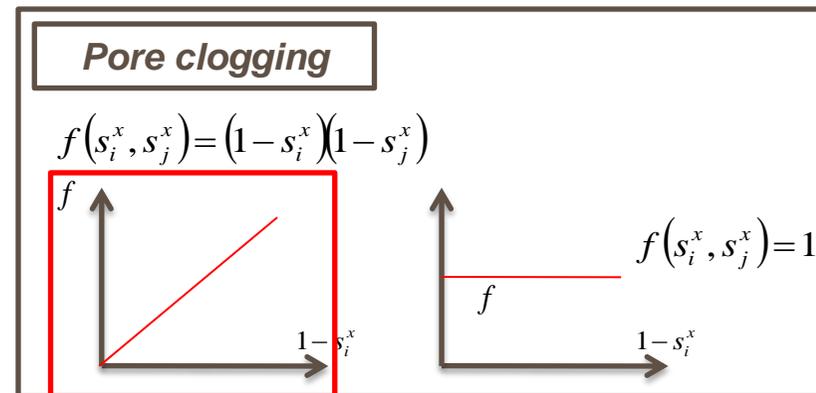
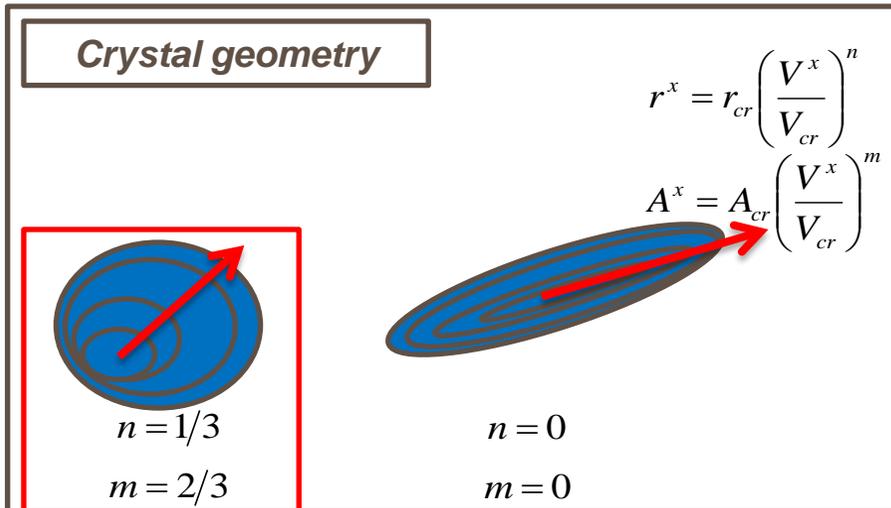
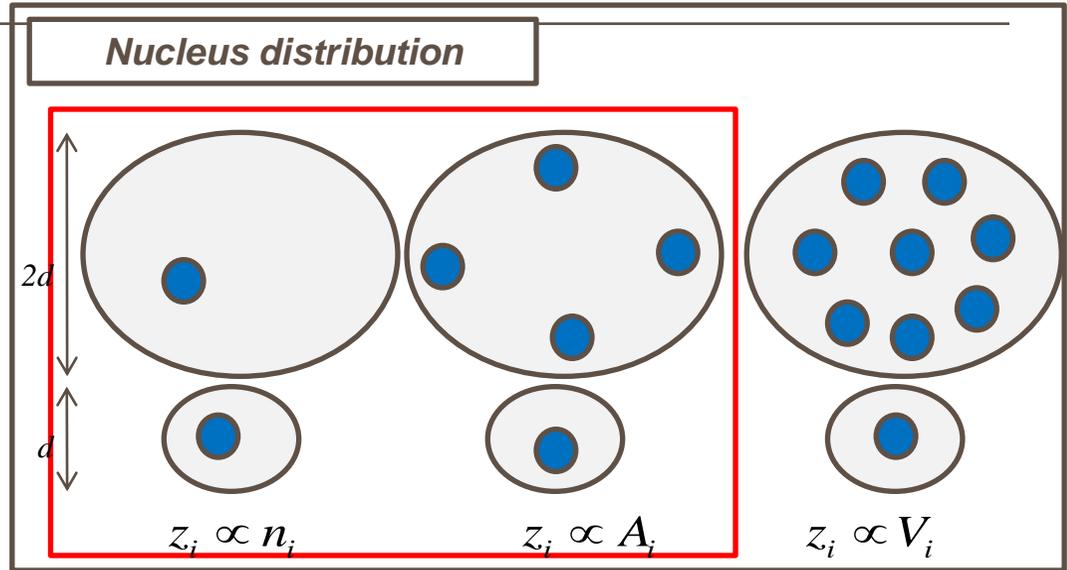
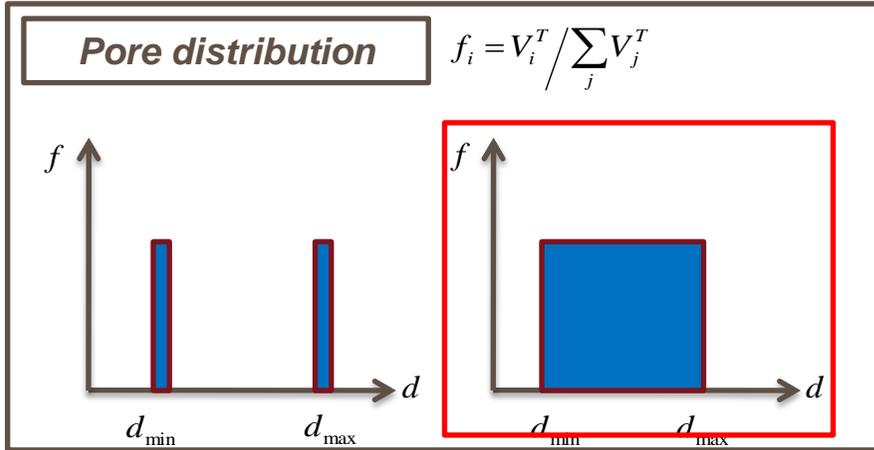
Description of one case



- Volume fraction of crystal in pores
- Effective pressure in pores [Mpa]

Abdusalam Aili, 2012

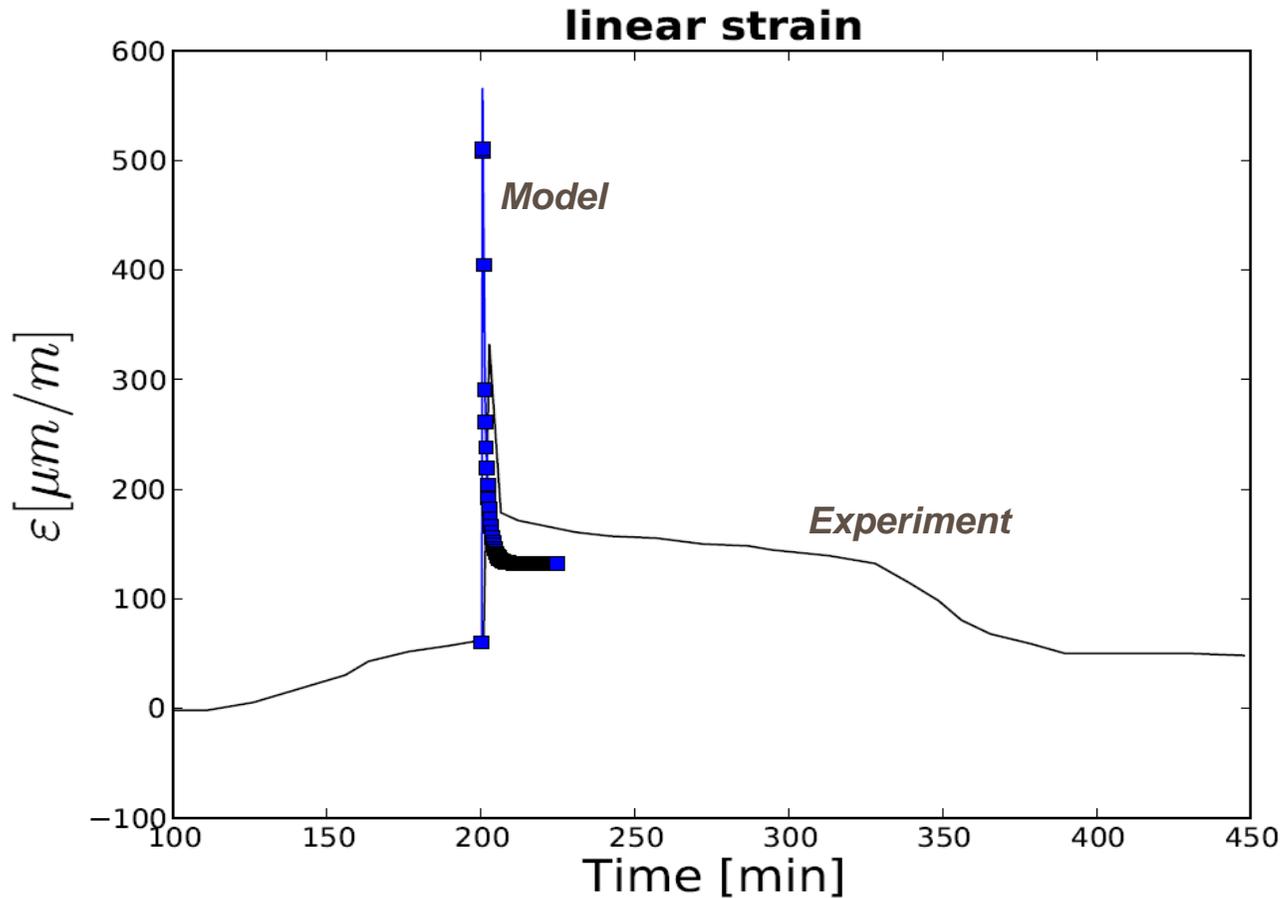
Parameters necessary to capture Espinosa – Scherer experiment



Crystallization & diffusion

Application to Espinosa & Scherer experiment

- Crystallization of mirabilite



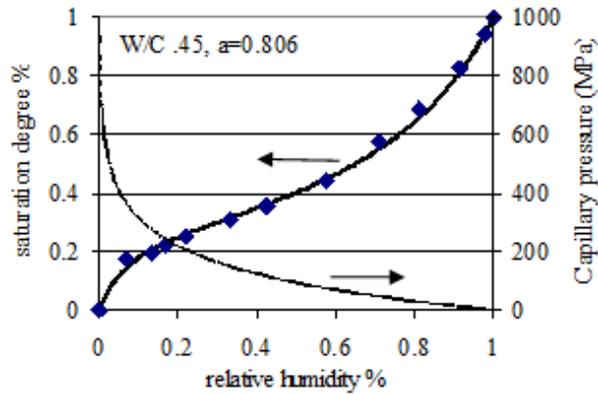
Diffusion coefficient

$$D = 10^{-10} \text{ m}^2 / \text{ s}$$

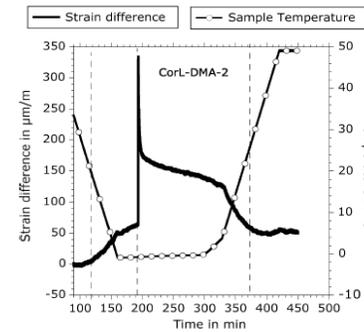
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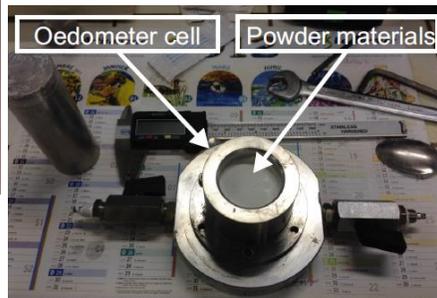


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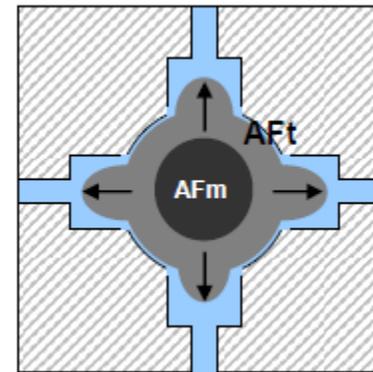


(Espinosa-Scherer, 2008)

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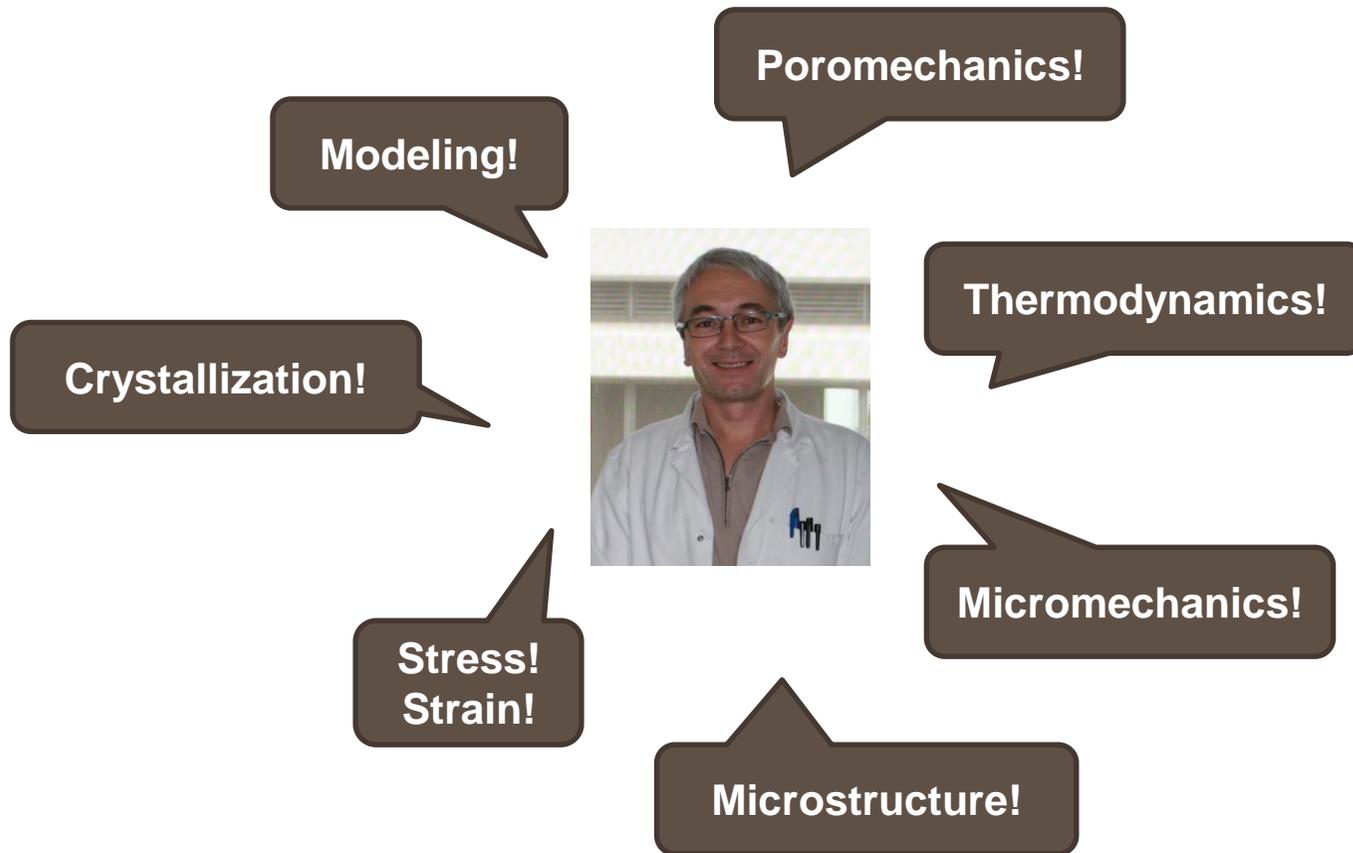


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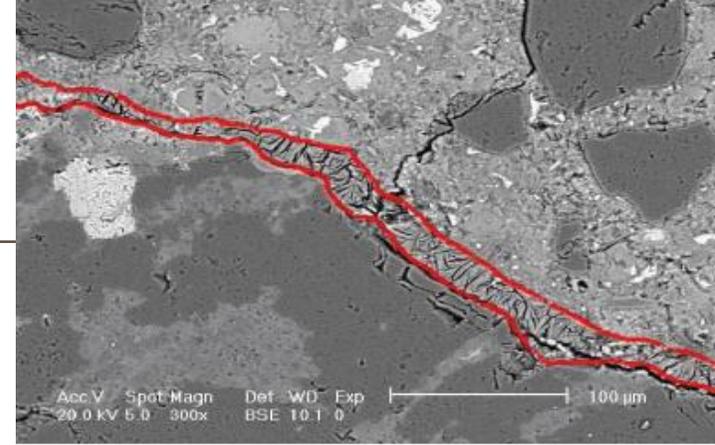
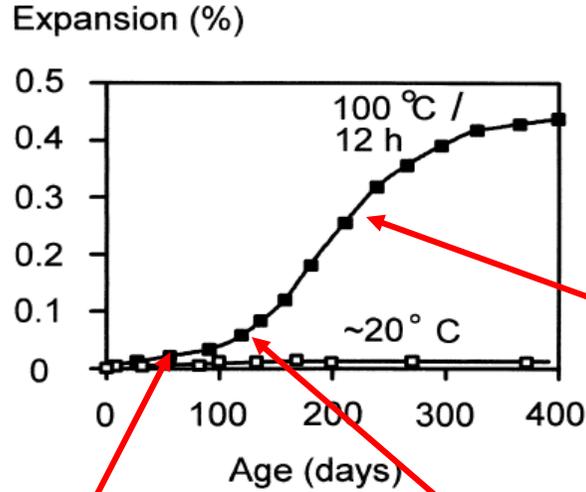


The day Gilles put pressure on me...

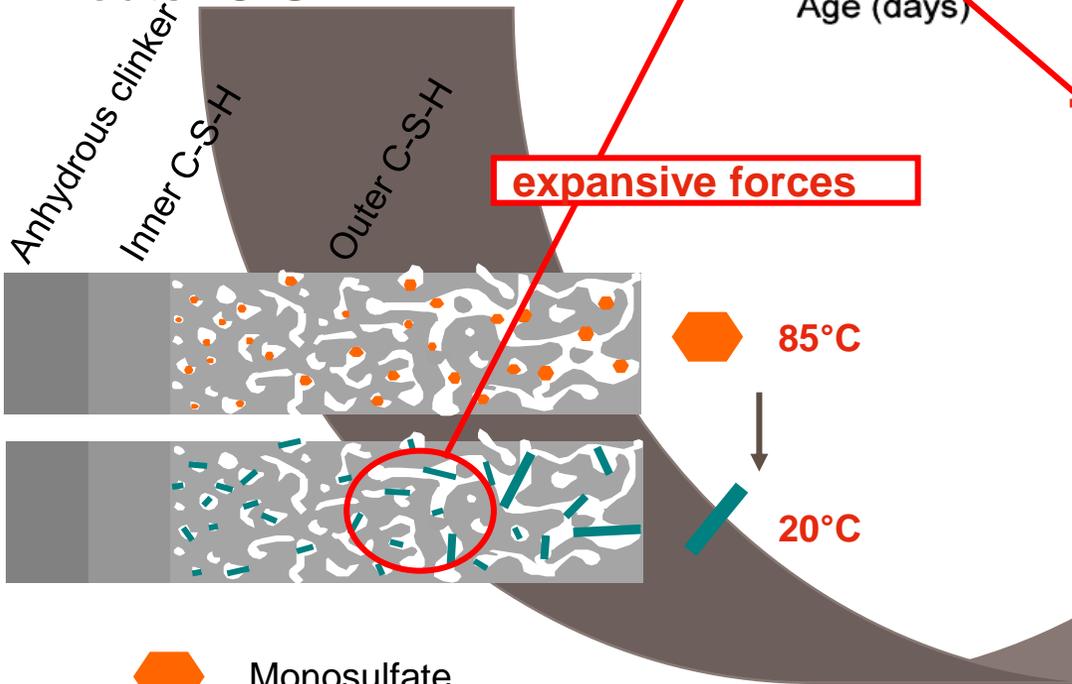
Mechanics and Physics of Porous Solids (MPPS) - A tribute to Prof. Olivier Coussy



A possible scenario for DEF

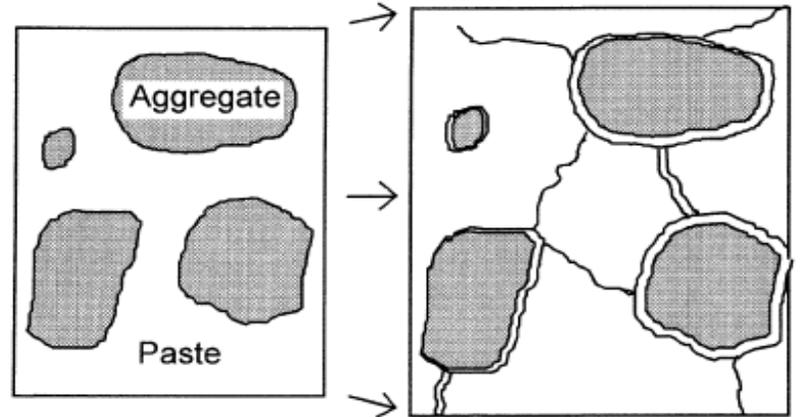


• **Initial state** :
ettringite precipitates
in outer C-S-H



• **Final state** : Ostwald ripening
localizes ettringite in large space

• **Threshold stage** : uniform paste
expansion creates damage and gaps
around aggregates

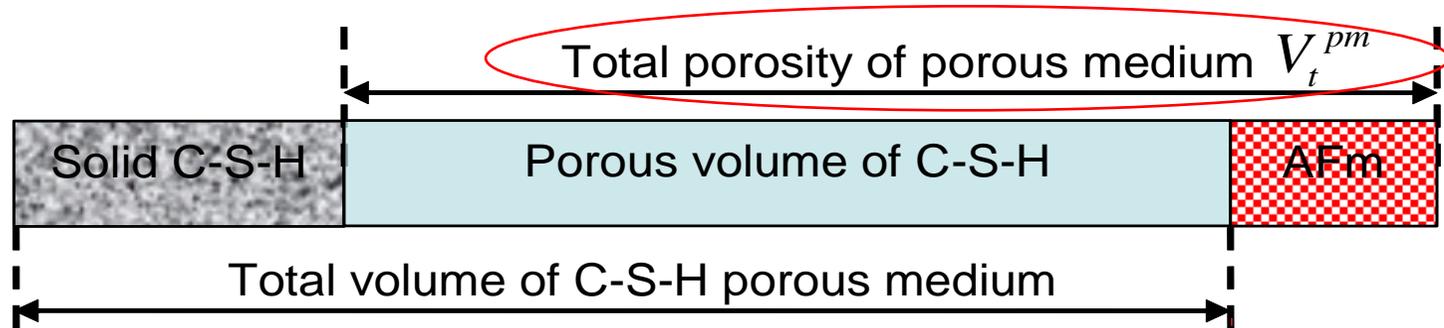


Monosulfate

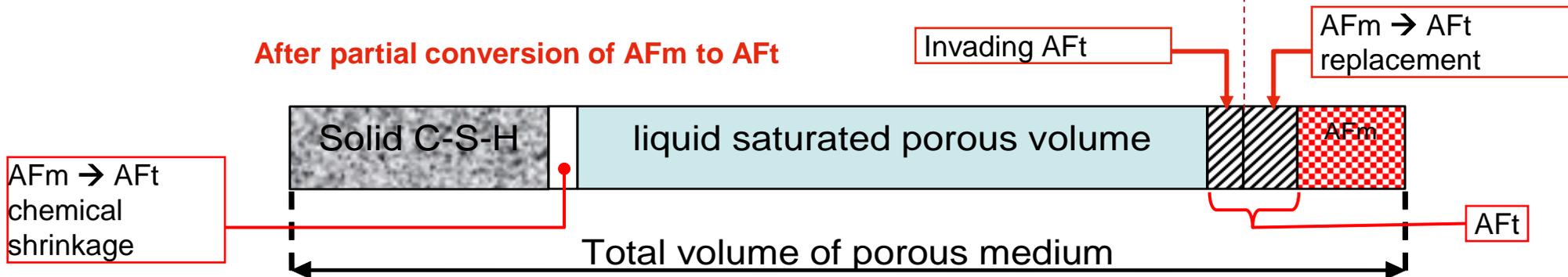
LafargeHolcim
Ettringite

A scenario for ettringite precipitation

Initial state, after hydration at high temperature

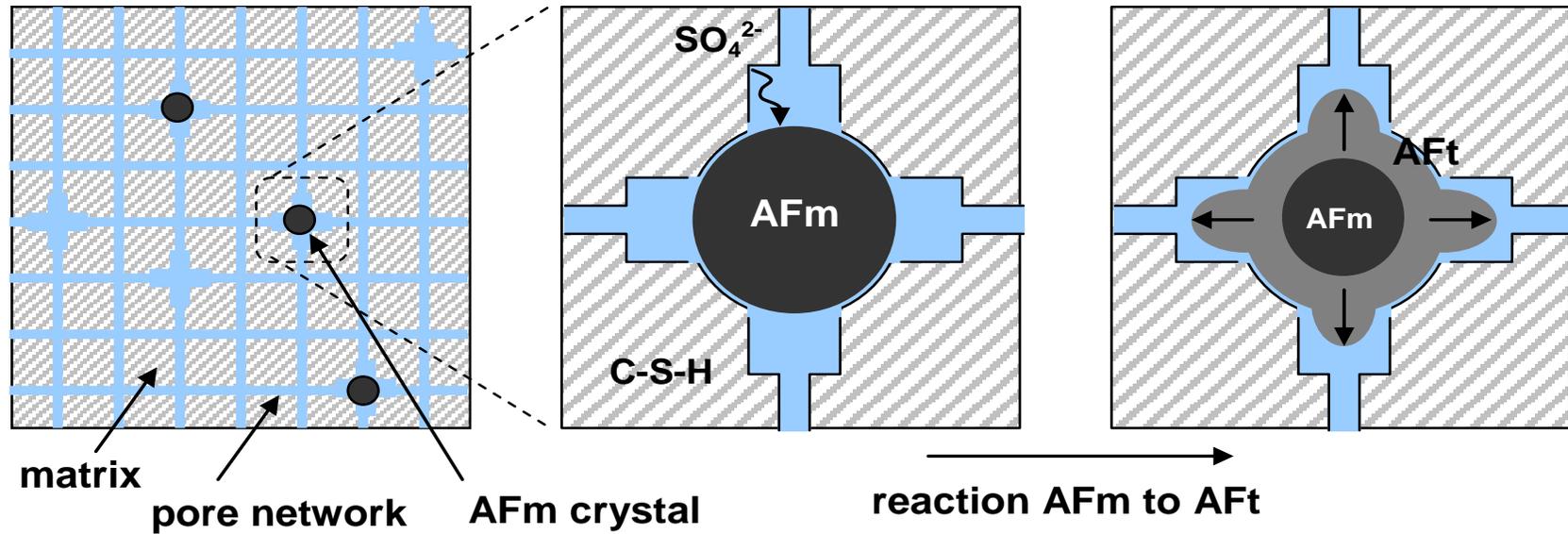


After partial conversion of AFm to AFt



- AFm phase is considered as a pore volume filled with reactive AFm crystals.
- AFm crystals are considered inert from a mechanical point of view.

How could ettringite precipitation generate strains?



Elastic energy stored by the solid phase

- Considering linear isotropic poroelasticity and isothermal and non-dissipative conditions, elastic energy is given by:

$$W = \frac{1}{2} \frac{\left(\sigma + \sum_{J=L,G,C,U} b_J \cdot (p_J - p_0) \right)^2}{K} + \frac{1}{2} \sum_{J,K=L,G,C,U} \frac{(p_J - p_0) \cdot (p_K - p_0)}{N_{JK}} + \frac{1}{2} \cdot \frac{s_{ik} \cdot s_{kj}}{2G}$$

- b_J , N_{IJ} are respectively the generalized Biot coefficients and the generalized poroelastic coupling modules. Assuming iso-deformation of porous media, we obtain:

$$b_J = b S_J \quad \text{with} \quad b = 1 - \frac{K}{k_s} \quad \frac{1}{N_{JK}} = \frac{S_J S_K}{N} \quad \text{with} \quad \frac{1}{N} = \frac{b - \phi_0}{k_s}$$

- Adopting a Mori-Tanaka homogenization scheme considering the porous material as formed of spherical voids embedded in a homogeneously strained solid matrix, bulk modulus K is given by:

$$K = \frac{4g_s k_s (1 - \phi_0)}{3\phi_0 k_s + 4g_s}$$

Note that in this equation,
AFm is considered as porosity
(non active mechanically)

Elastic energy stored by the solid phase

- If the material is unloaded at the macroscopic scale so that $\sigma = s_{ij} = 0$, the elastic energy stored becomes:

$$W = \frac{1}{2} \left[\frac{b^2}{K} + \frac{(b - \phi_0)}{k_s} \right] [S_C \cdot \Delta p_C + S_L \cdot \Delta p_L]^2$$

- where

- $\Delta P_J = p_J - p_0$ with p_0 the atmospheric pressure
- gas pressure remains at atmospheric pressure

- Considering cement paste as a brittle material, it can be stated that it cannot store elastic energy beyond a critical threshold.
- In the case of a mean isotropic tensile stress σ ($s_{ij}=0$) and without internal pressures ($p_J - p_0 = 0$), the elastic energy is given by:

$$W = \frac{1}{2} \frac{\sigma^2}{K}$$

Hypotheses for material behaviour

- Equalling stored elastic energy from internal pressures and from isotropic tensile stress, the macroscopic tensile stress can be expressed as a function of internal pressures and saturation degrees:

$$\sigma = \sqrt{\left[b^2 + (1-b)(b - \phi_0) \right]} (S_C \cdot \Delta p_C + S_L \cdot \Delta p_L)$$

- It is interesting to remark that capillary pressure and crystallization pressure play obviously the same role, weighed by saturation degrees.
- However, signs of these pressure terms are opposite (liquid phase will be under tension while crystal phase will be in compression). Consequently, they act in opposite ways from viewpoint of energy.

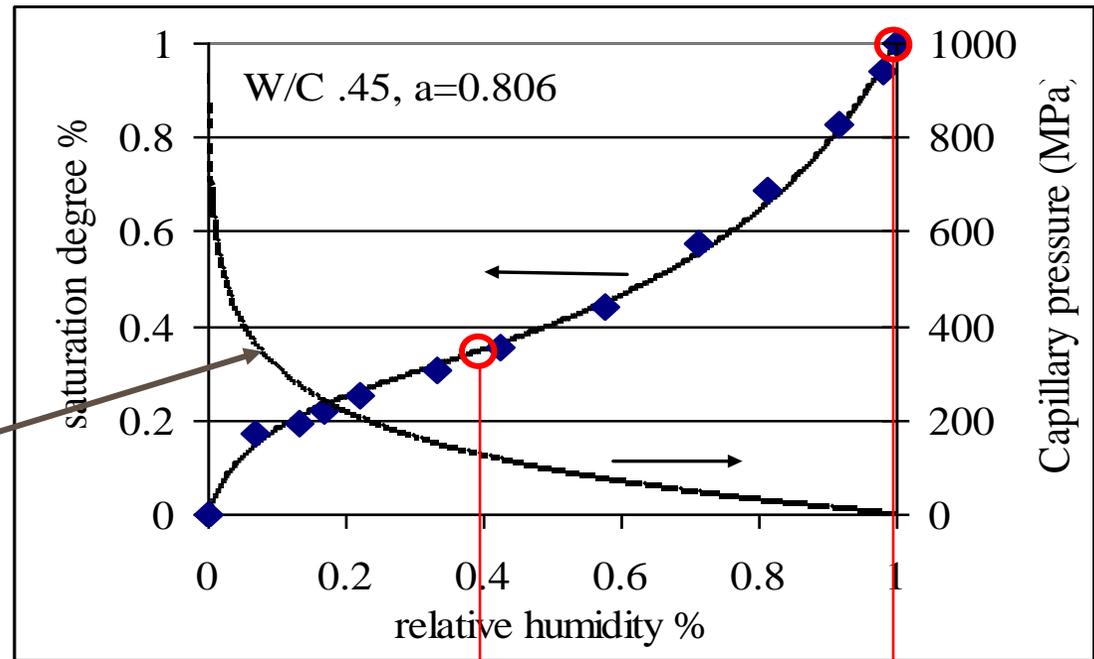
Computing pressures

Crystallization pressure

$$p_C = -\frac{\gamma_{CL}}{\gamma_{GL}} p_L$$

Capillary pressure

$$\Delta p_L = p_L - p_0 = \frac{-RT}{v_w M_H} \cdot \ln(RH)$$



$C_{1.7}SH_{2.5}$

$C_{1.7}SH_4$

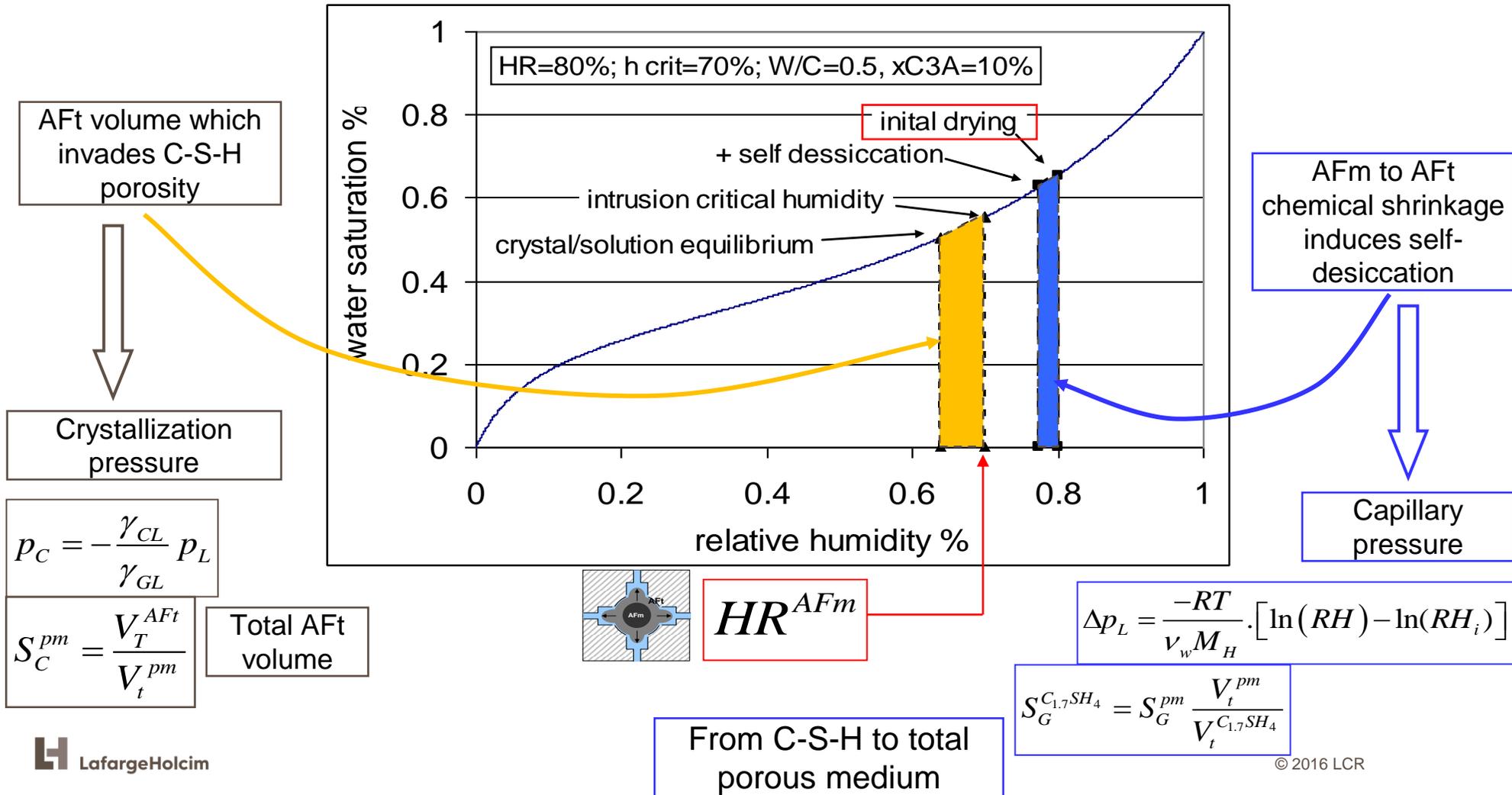
+ free water

Data Powers & al. 1948

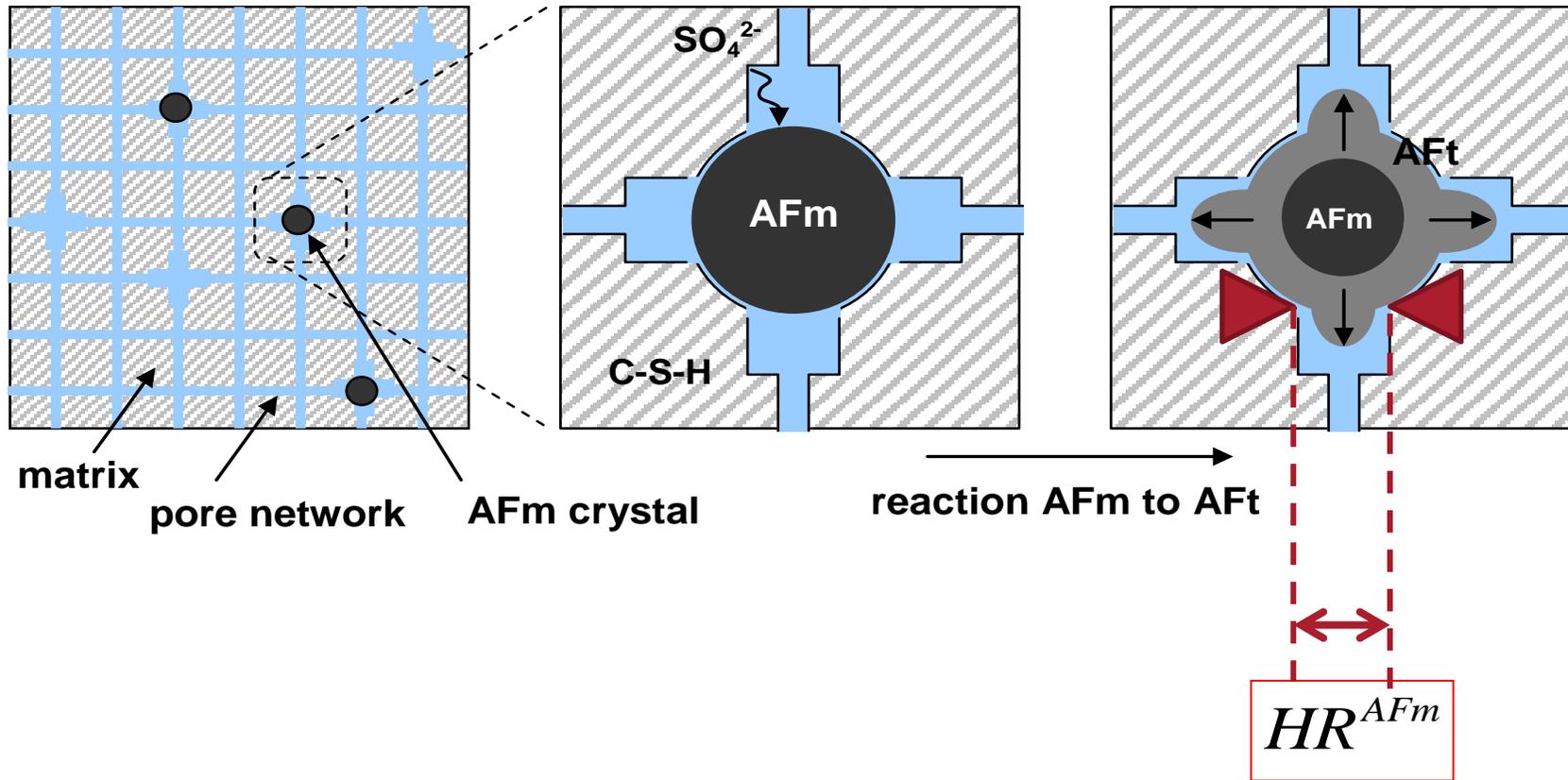
Deduced from a simple $C_{2.7}S$ hydration model

Integrating over the whole pore distribution

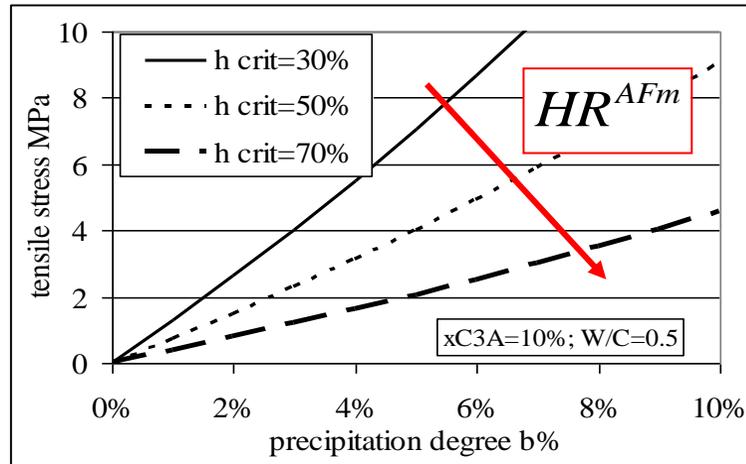
- Input parameters : x_{C3A} , w_0/c_0 , initial drying state, intrusion critical humidity, precipitation degree β



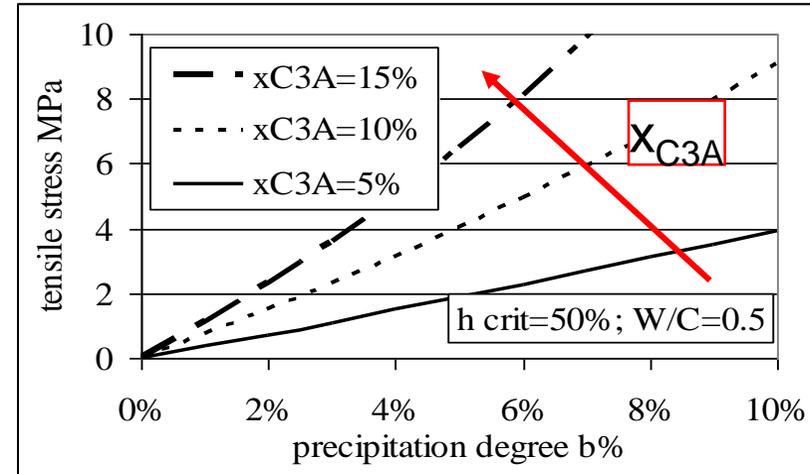
'intrusion critical humidity'?



Tensile stress resulting from DEF could lead to damage even for low value of conversion of AFm to AFt

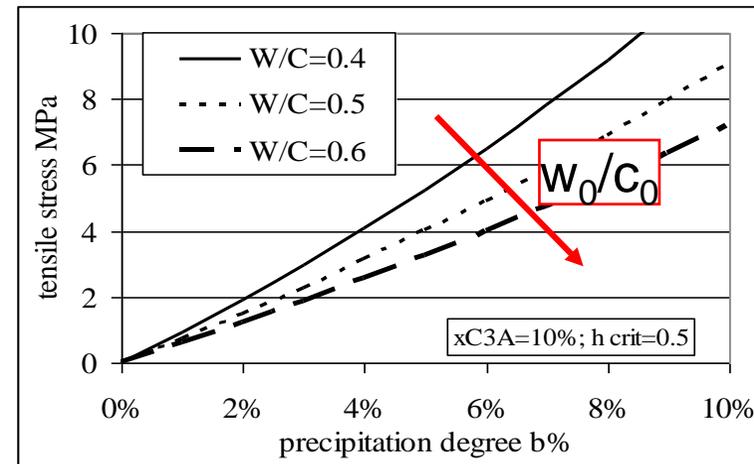


Effect of intrusion radius



Effect of C_3A content

- The first order factors are
 - intrusion radius HR^{AFm}
 - C_3A content



Effect of w_0/c_0 ratio

Back to Gilles...

- Gilles could swallow a huge amount of papers, on which he built a personal framework for understanding concrete
- He had a passion for the work of his predecessors, but was also up to date for very recent research
- Gilles was at ease with complex concepts and equations, able to develop models
- But he was always careful about how this could help practically, on the field



Hi Rémi, it's Gilles, I've stopped on a parking lot, thinking about our great discussion this afternoon, I just hope you don't 'Bolomey' too much!

So I was thinking, all that we say about models and tools, I believe it's a matter of pedagogy. I wonder if we shouldn't define some '10 golden rules level 0', '10 golden rules level 1' etc.

I mean, giving people the capacity to act by themselves rather than giving them models. I like the gel-space ratio approach, it's a nice model, but people don't understand what's behind. Shouldn't we explain and tell people 'do it by yourself now', 'you've understood that...'. .

Well, that was my thoughts while driving. So, have a good night, and see you tomorrow, ciao!





Merci !