Multiscale imagery of cement paste:

relation with the confined transport of water

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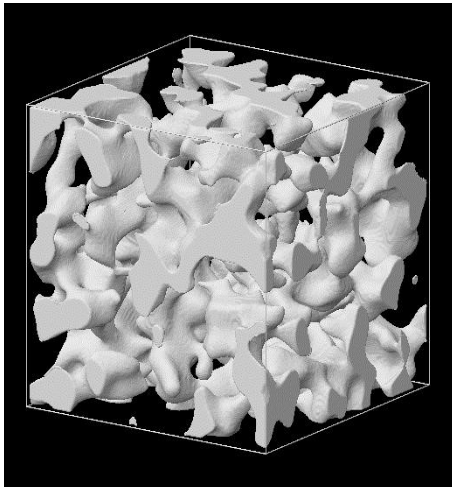
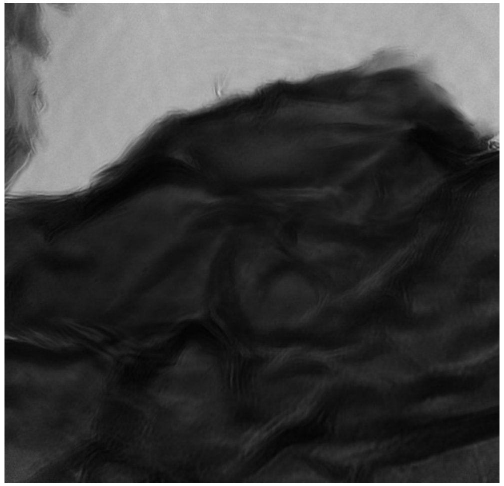
NUMEROUS POROUS MATERIALS HAVE A MULTISCALE STRUCTURE

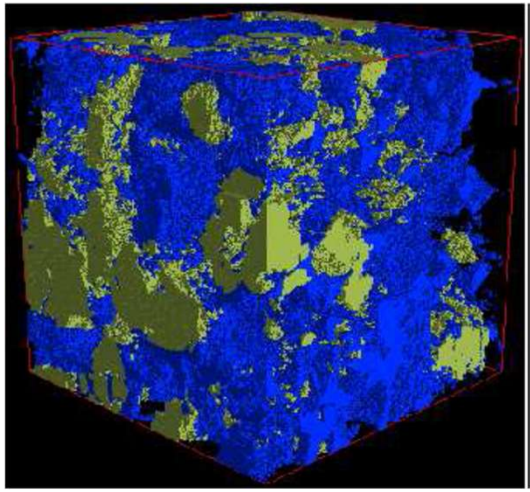
Porous ceramics and catalyst



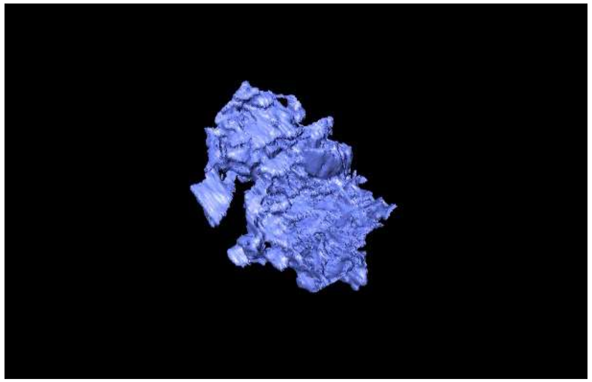
Clay suspensions and cakes



Geo-pore network



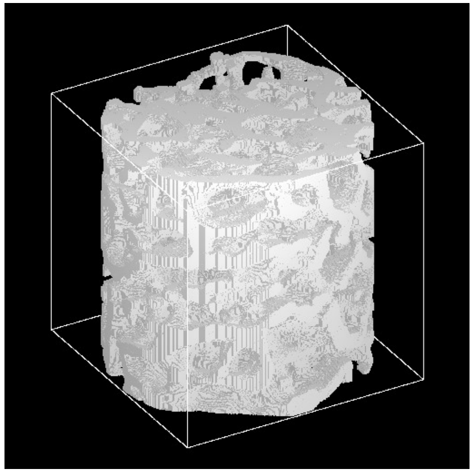
Building material



(CSH grain)

plaster

Bio tissues (Bone, Biofilms…)



CHALLENGES

CSH is a multiscale complex structure

Questions: Is there a length scale more specific for:

- **The mechanical strength ?**

- **The long term transport of ions and water molecules ?**

Menu :

PART I: Get geometrical information (2D and 3D) of the mesoscale structure ranging from the nanometer (if possible) to the micrometer lengthscale.

PART II:

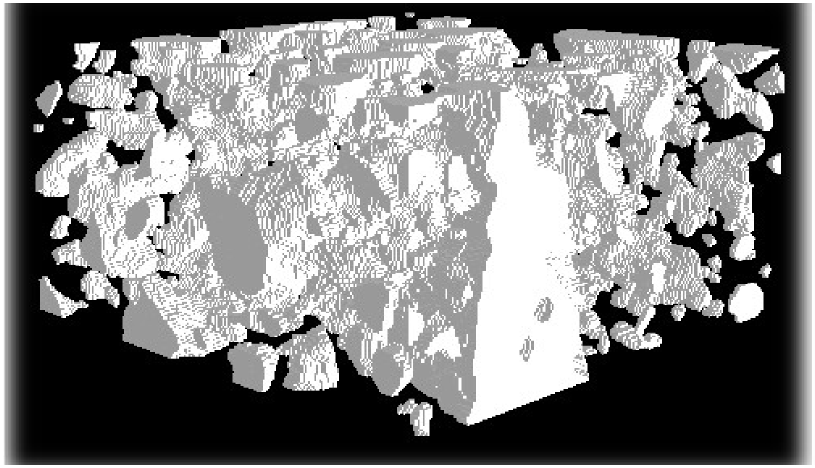
- Generate tractable but constrained geometrical models to analyse long term molecular transport (confined diffusion and adsorption)

- Identify at the mesoscale, factors influencing the fluid dynamics.

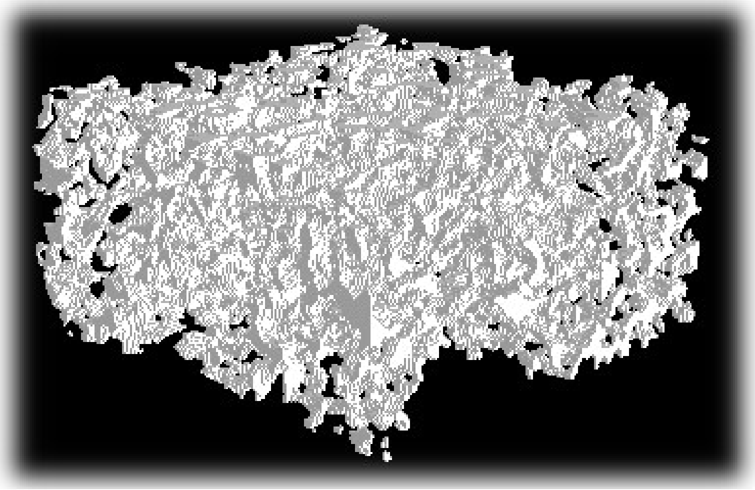
PROBING THE MICROSTRUCTURE (at the μm Scale)

μCT Cement paste during setting (TOMCAT-SLS)
Voxel resolution: 0.7 μm

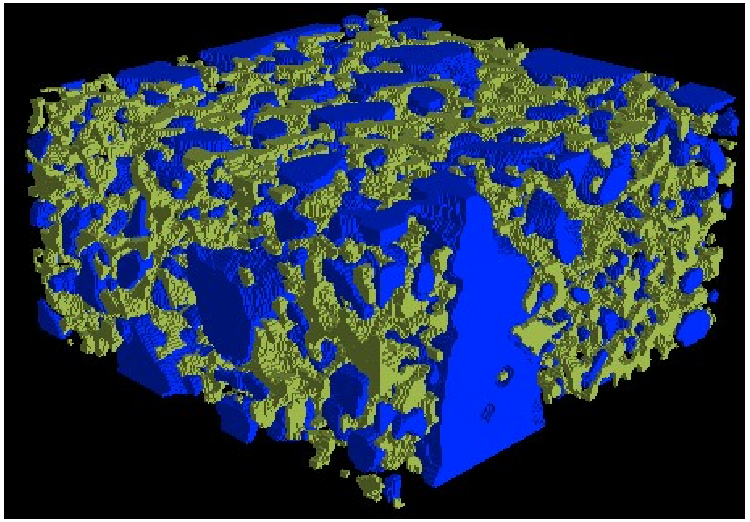
Unreacted grains



Hydrated phase



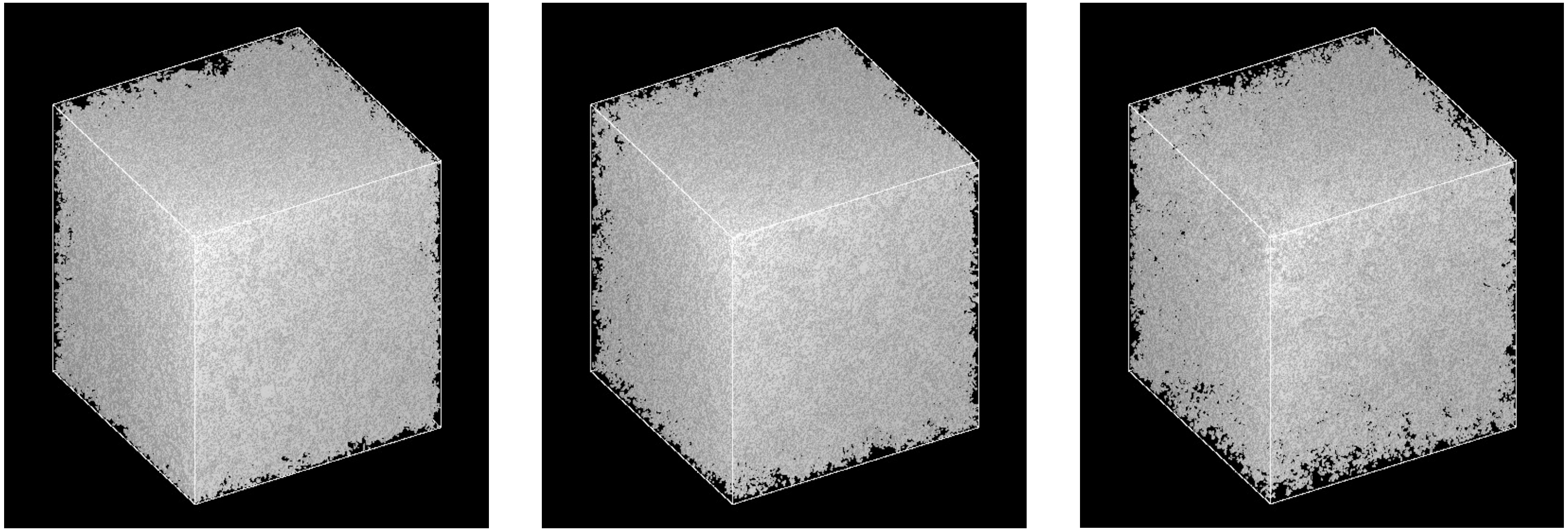
Capillary pore network



Eur. Appl. Phys. (2012) 60: Phys. J. 24202

We could believe what we see ,

34H 83 H 150H

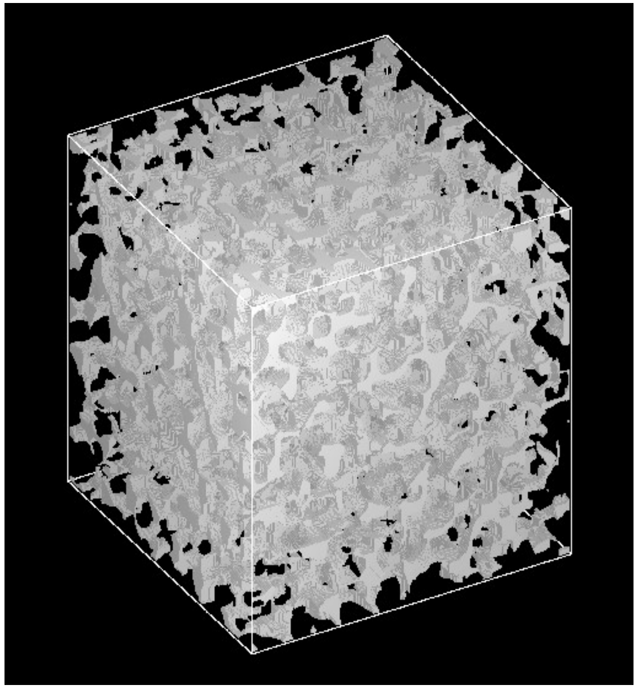


Time evolution of the capillary pore network of the cement paste (resolution 0.7μm)

But with modern imaging techniques,

what we see is beginning to be very complex !

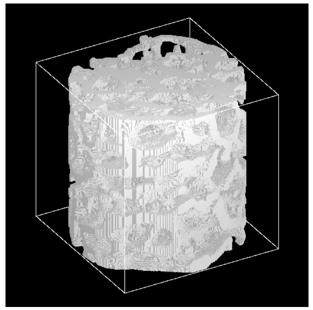
The pore network topological graph:



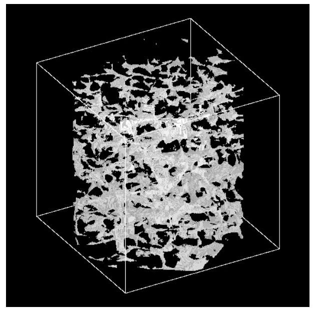
Connexion factor,
an intensive parameter:

$$C_T = -\frac{(\alpha_{0,I} + \alpha_{0,c} - \alpha_1)}{(\alpha_{0,I} + \alpha_{0,c})} \qquad -1 < C_T$$

$0 < C_T$



Percolation $C_T \approx 0$



$-1 < C_T < 0$

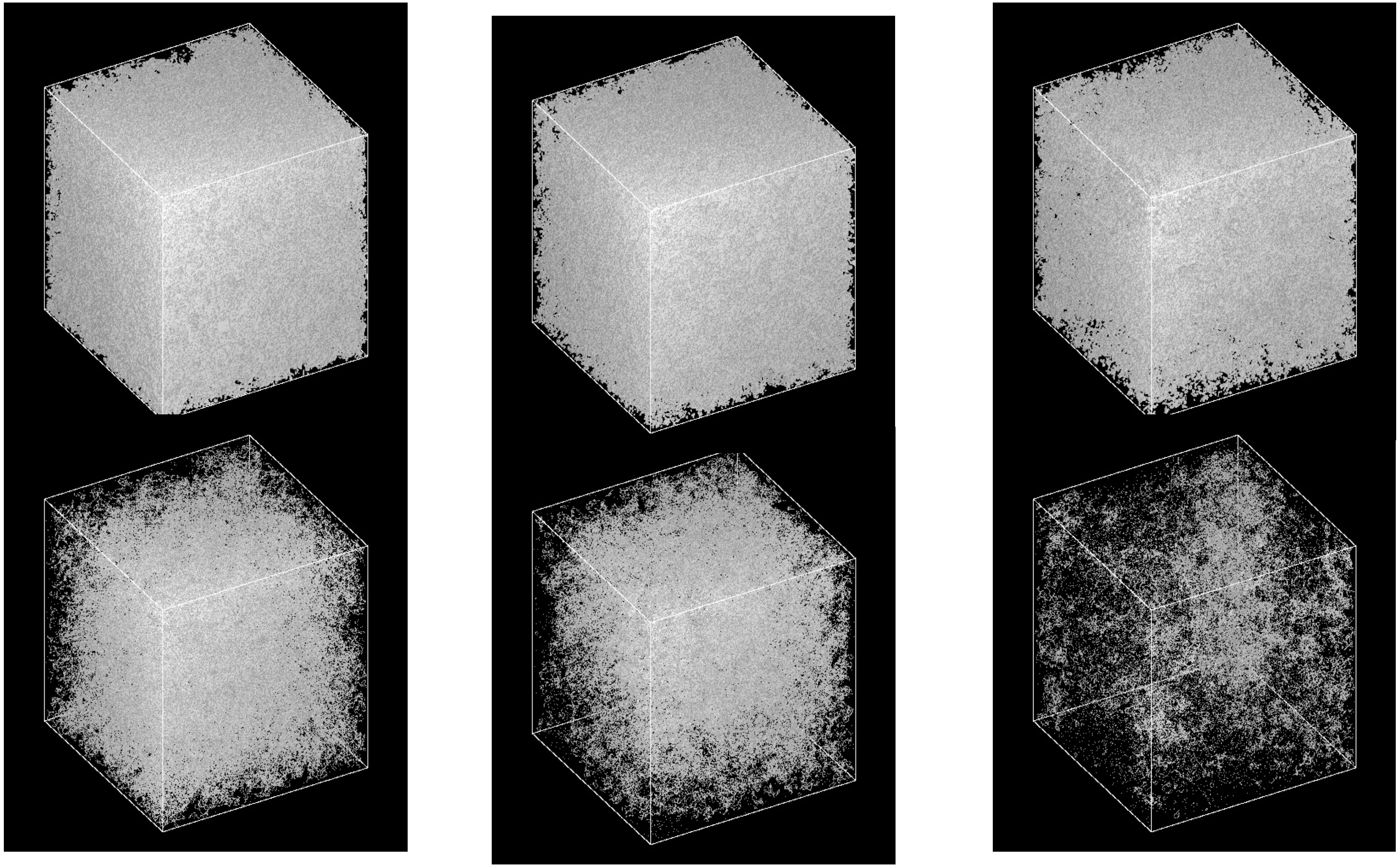
J. of Microscopy, 199,149 -161(2000) **Eur. Appl. Phys. (2012) 60: Phys. J. 24202**

Time evolution of the 3D capillary pore network of the cement paste

Microtomographies and their retraction graphs

(Voxel resolution 0.7μm)

34H | 83 H | 150H



Eur. Appl. Phys. (2012) 60: Phys. J. 24202

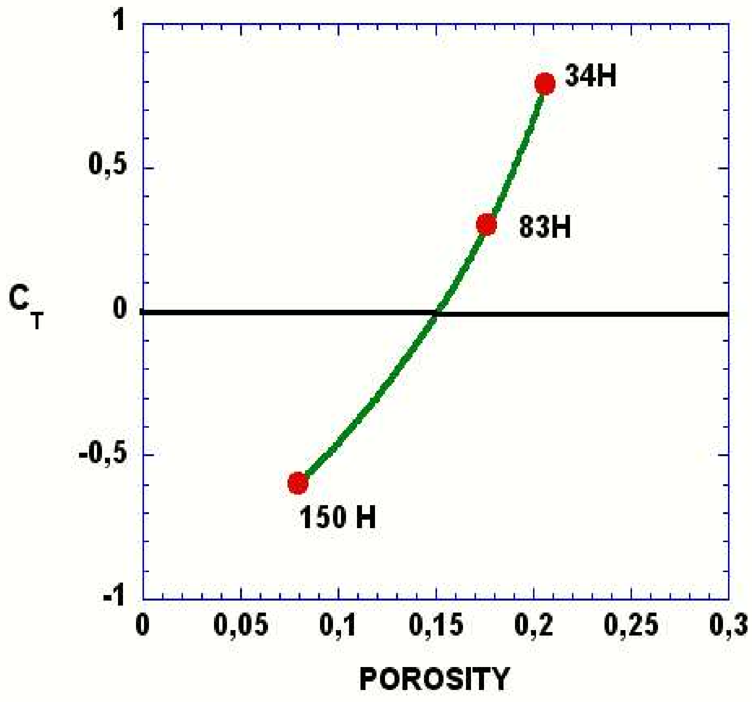
Evolution of the capillary pore network

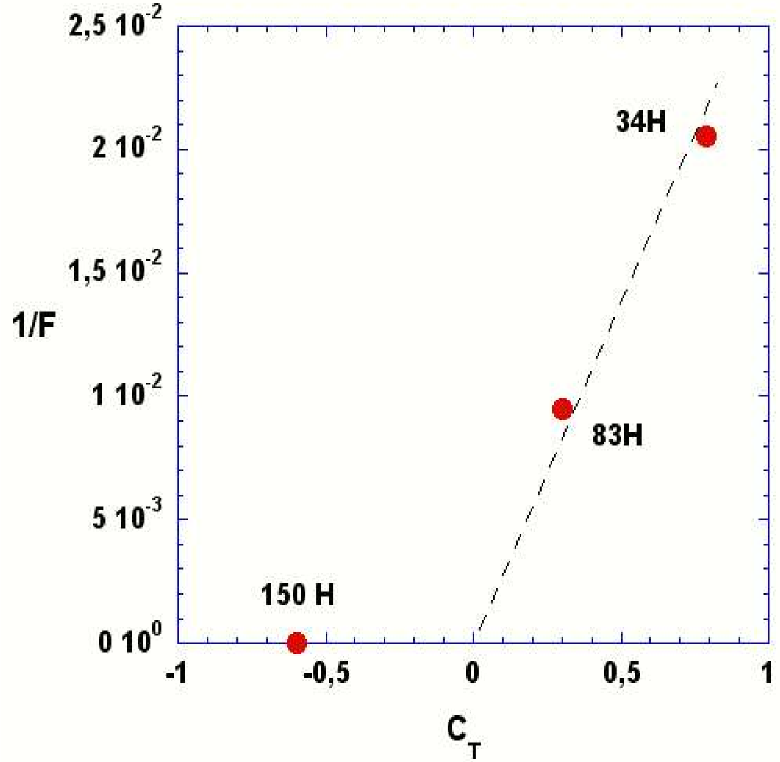
Simulation of the electric transport

F: Formation Factor

Topological evolution

$$F = \frac{R_{Porous--sample+brine}}{R_{brine}}$$





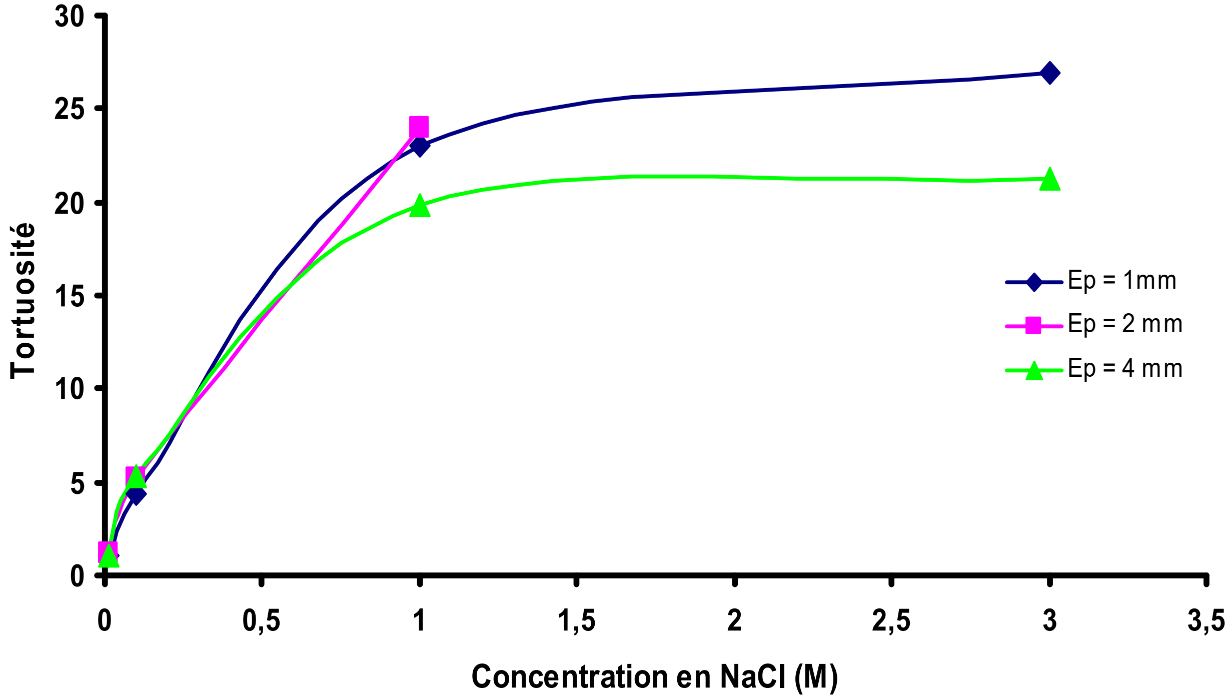
Eur. Appl. Phys. (2012) 60: Phys. J. 24202

HOWEVER:

Electric conductivity:

Evaluation of the electric tortuosity at hight ionic strength

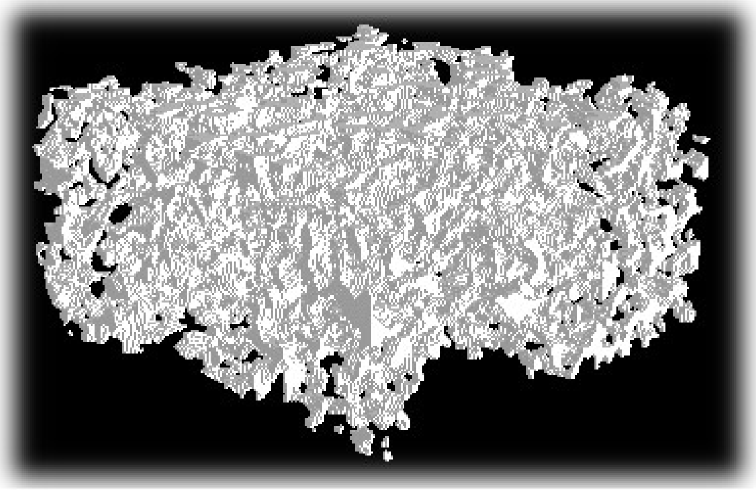
CEM I, LCPC, 1.5 year old



$$Tortuosity = T = \Phi F$$

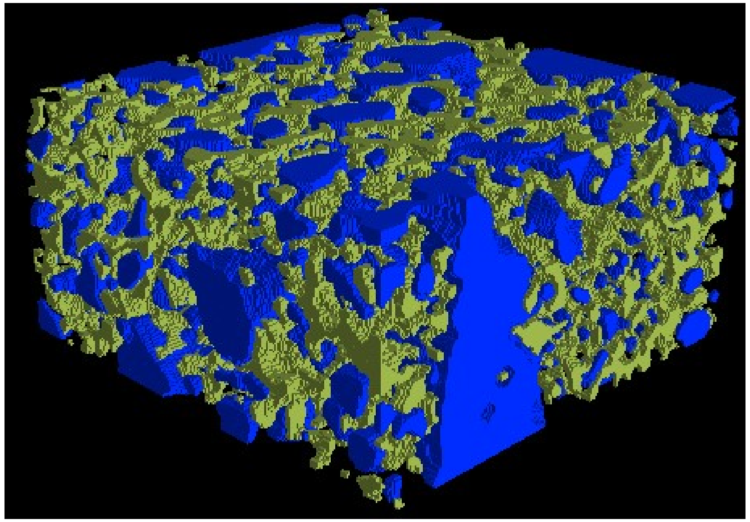
H. Chemmi et al Eur. Phys. J. Special Topics 224, 1749–1768 (2015)

INTERMITTENT REGIME OF DIFFUSIF/ELECTRIC TRANSPORT



Hydrated phase

micropores-nanopores transfer



Capillary pore network

Probing CSH structure at the nanoscale

ONE POSSIBLE TOOL : the X-Ray Full field microscopy

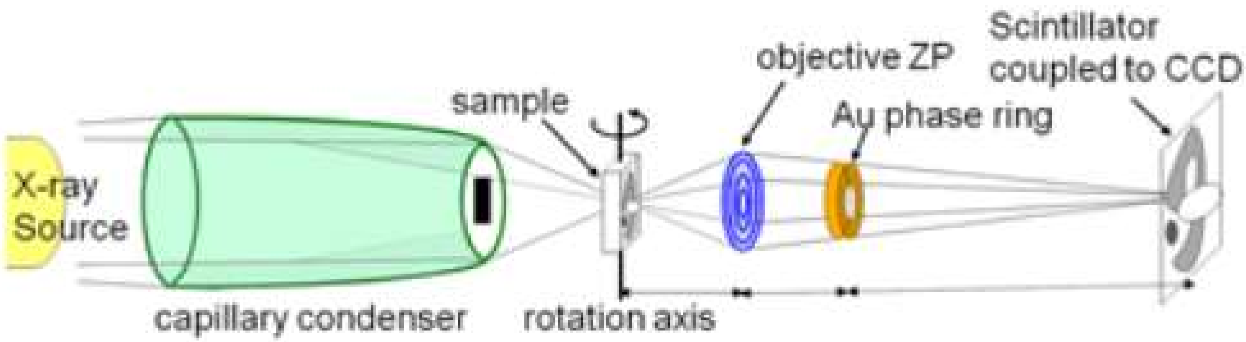


Figure: Xradia

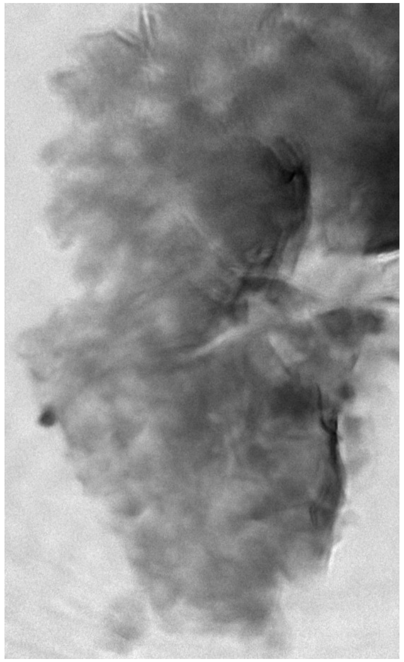
- Incoherent illumination
- Phase contrast through phase ring (Zernike)
- Resolution down to 30 nm
- Images immediately available
- Commercial solutions exist

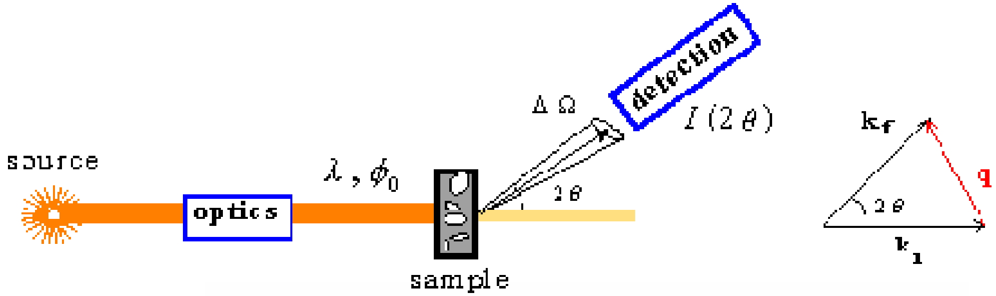
Probing CSH structure at the nanoscale

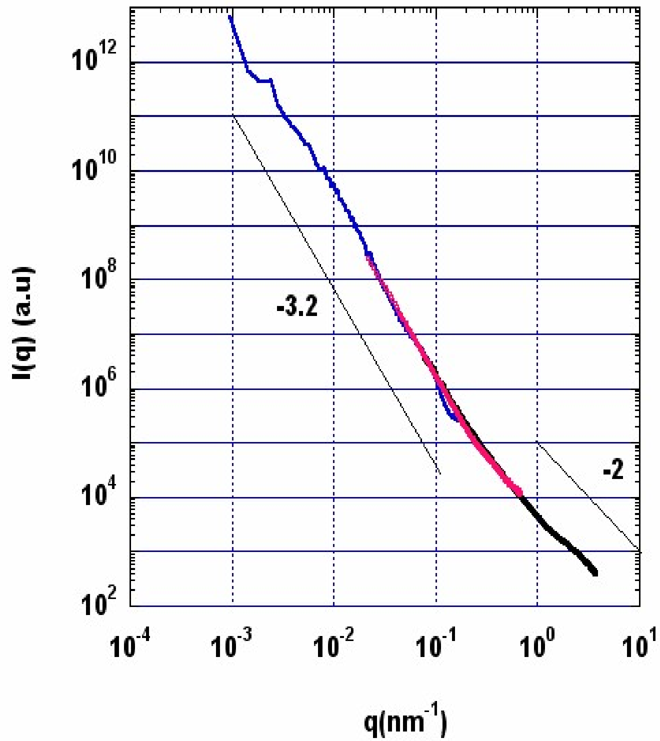
Small Angle Scattering versus TXM

TXM

Pixel size= 10 nm

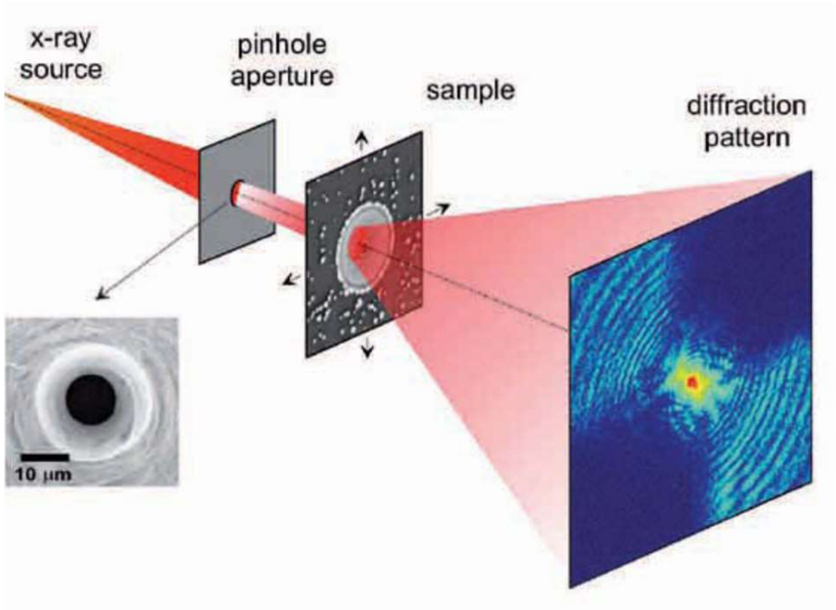




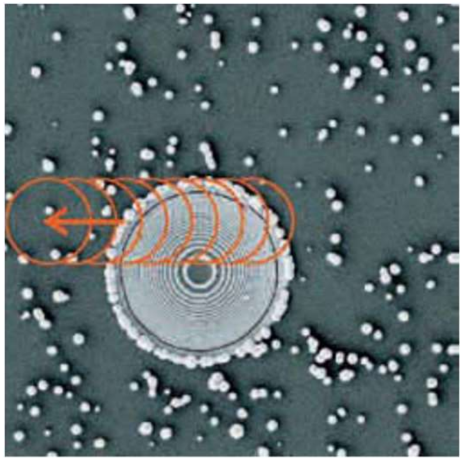


AMERICAN MINERALOGIST Volume: 97 Issue: 2-3 Pages: 480-483 2012

HIGHER RESOLUTION: PTYCHOGRAPHY & LENSLESS X-RAY IMAGING



Results with X-rays. (a) Scanning electron micrograph of the test sample with gold nanostructures. The circles indicate nine of the 225 pinhole positions for which diffraction patterns were recorded (Fig. 2). (b) Phase of the reconstructed complex-valued exit wave of the specimen (linear colour scale). The images represent a field of view of 52 x 52 µm2.

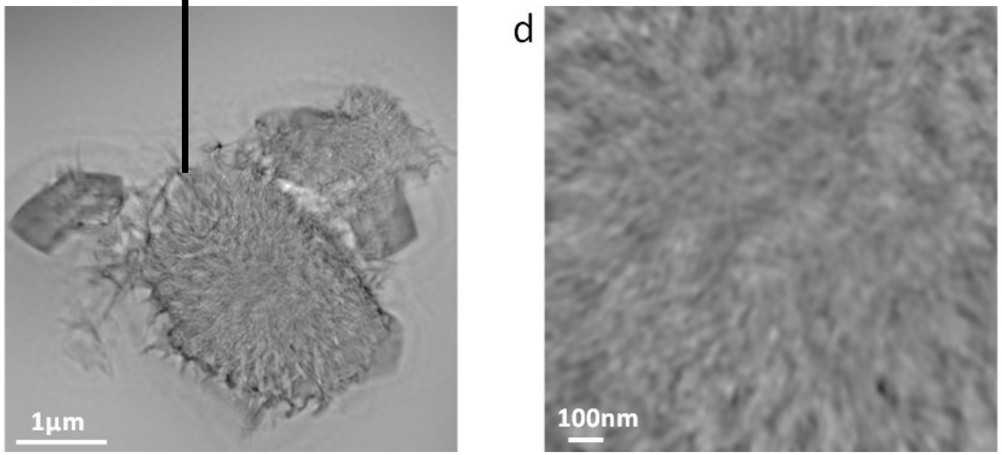


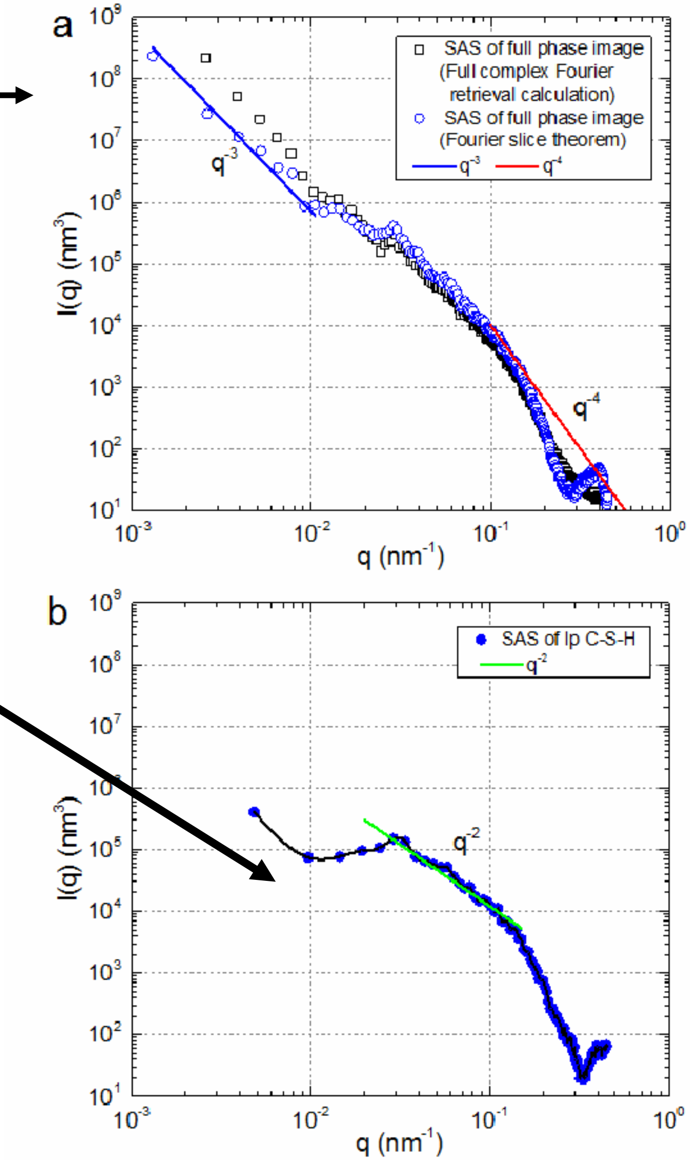
M.A. Pfeifer, G.J. Williams, I.A. Vartanyants, R. Harder, and I.K. Robinson, *Nature* 442, 63 (2006).

Soft X-ray Ptychographic Imaging and Morphological Quantification of Calcium Silicate Hydrates (C-S-H) at the nanoscale

S.Baea,, R. Taylor, D. Shapiro, P. Denes, J. Joseph, R.Celestre, S.Marchesini, H. Padmore,
T. Tyliszczak, T. Warwick , D. Kilcoyn, P. Levitz and P. J.M Monteiro

(J. Am. Ceram. Soc. june 2015)





resolution=5 nm

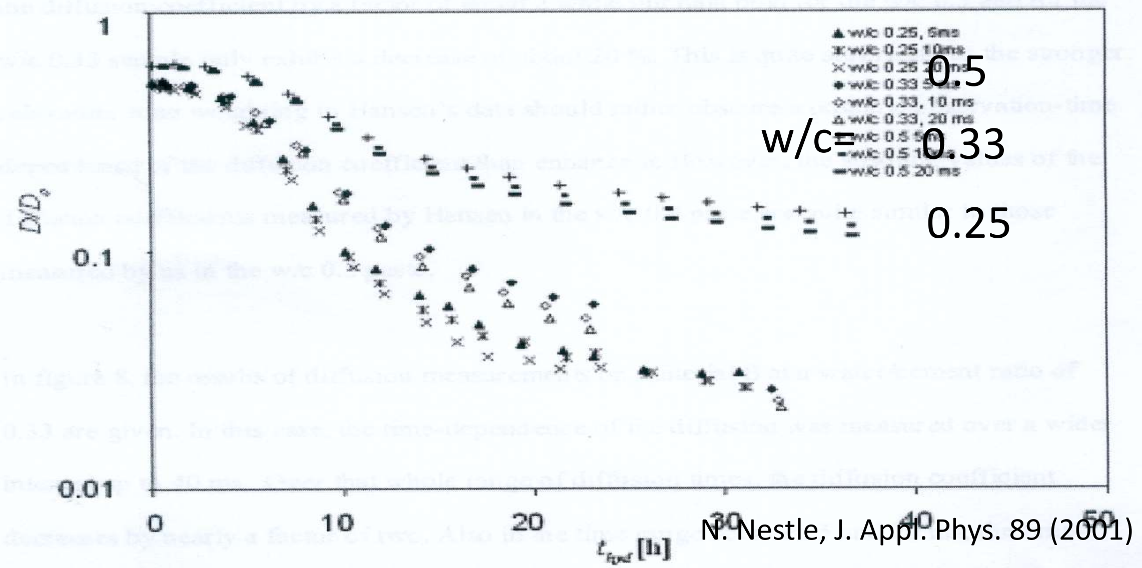
Outer CSH: q^{-3} signature :

Large distribution of diluted meso-macro pores

Inner CSH: q^{-2} signature :

PART II: ABOUT WATER DIFFUSIF TRANSPORT IN CSH

Strong reduction of the water molecular diffusion process in aged CSH



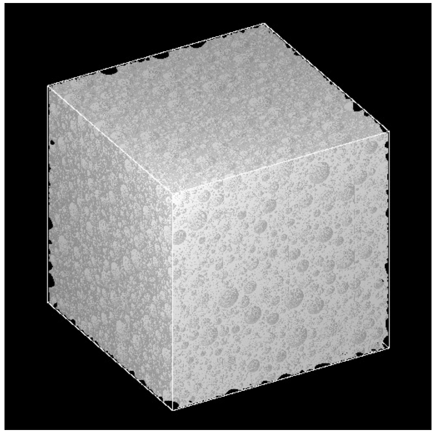
N. Nestle, J. Appl. Phys. 89 (2001)

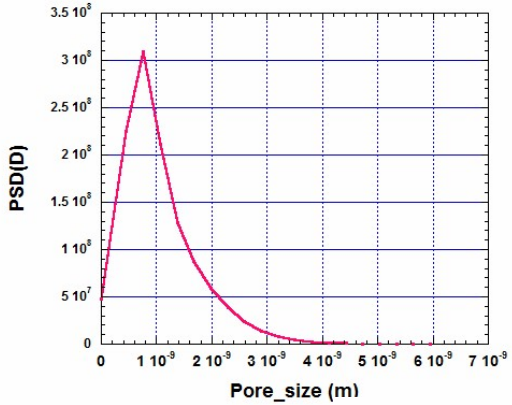
Figure 7. Water self-diffusion coefficients (relative to the diffusion coefficient of free water) measured in hydrating pastes of material A prepared at different water/cement ratios. Hydration temperature: 31 °C.

Tortuosity: $T = D_0 / D$ $\qquad T_r > 20$

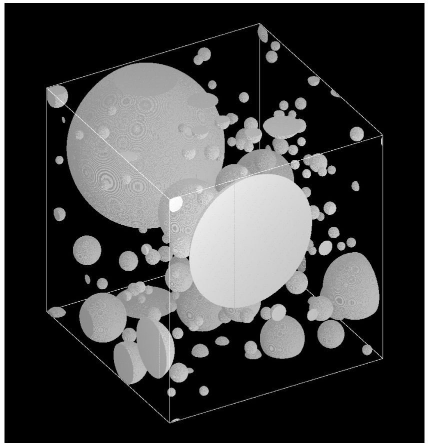
A FIRST NAIVE CONSTRAINED TOY MODEL (Size=150 nm)

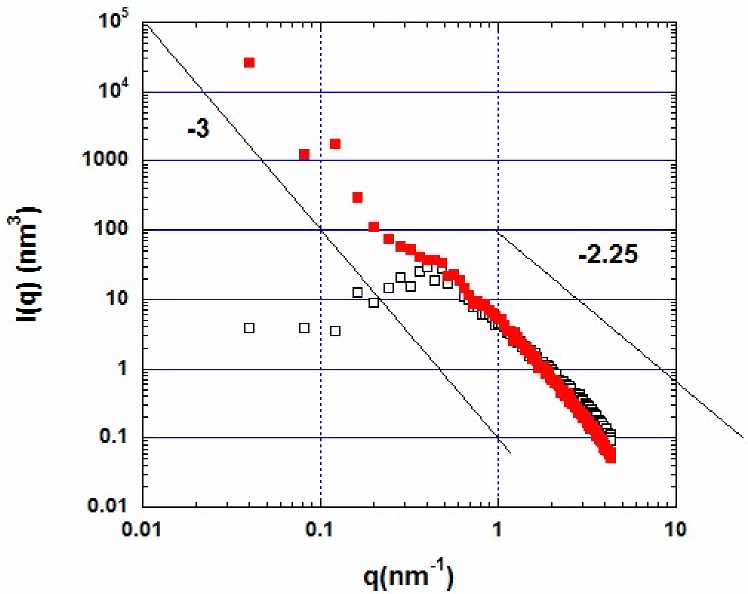
Dense association of strongly polydisperse nanospheres.
Accessible porosity for water=0.202



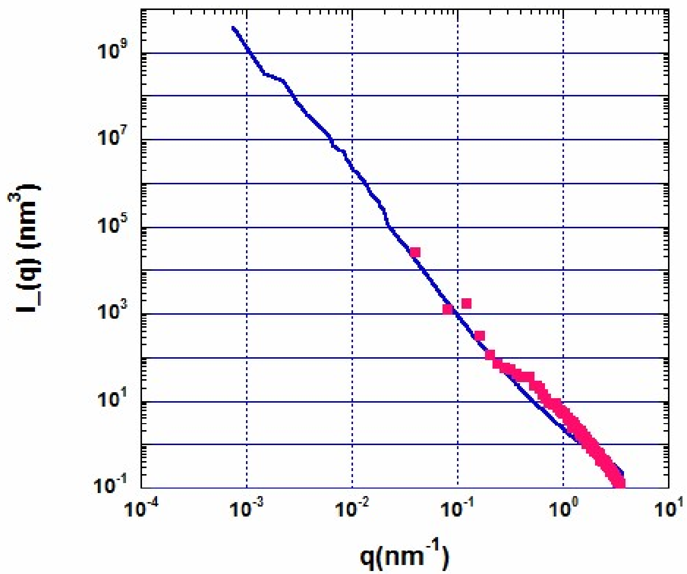


Disconnected mesopores
porosity=0.2



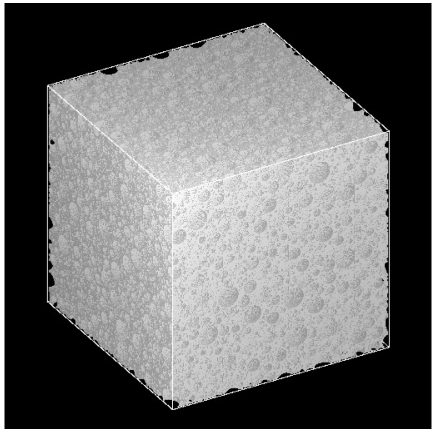


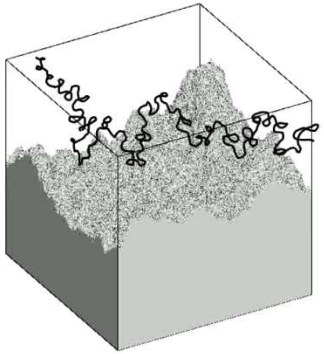
Comparison with exp

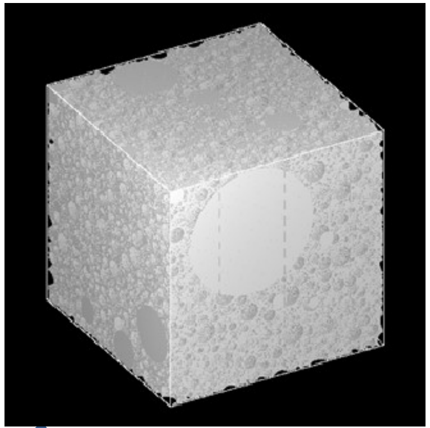


Confined diffusion and adsorption: An Internittent Process

$$D_0 = 210^{-9} m^2 / s$$

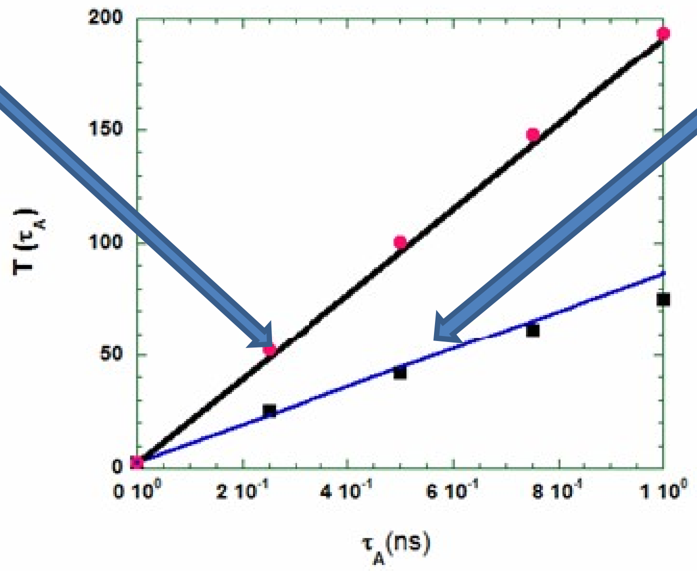






$$T(\tau_A = 0) = 2.5$$

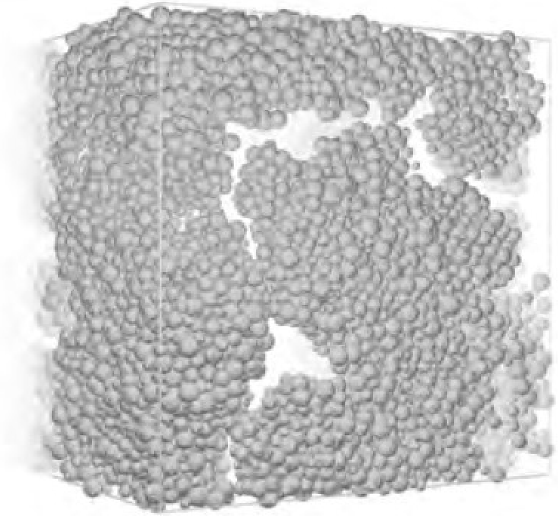
$$T(\tau_A = 0) = 2.4$$

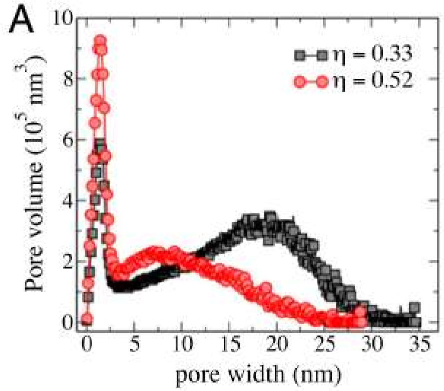


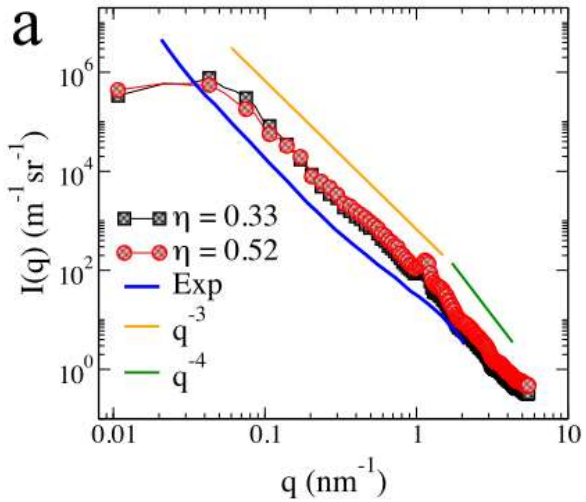
PNAS vol. 113 no. 8, 2029–2034, 2016

The mesoscale texture of C–S–H

Katerina Ioannidou * †, Konrad Krakowiak *, Mathieu Bauchy ‡, Christian Hoover *, Enrico Masoero §, Sidney Yip ¶, Franz-Josef Ulm *, Pierre Levitz ||, Roland J.-M. Pellenq * † **, and Emanuela Del Gado ††







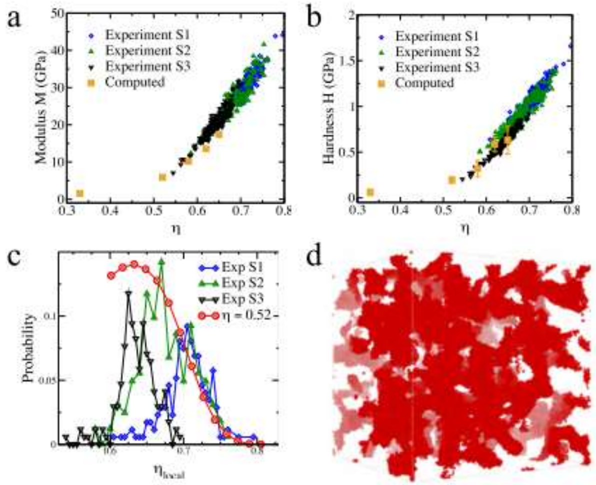
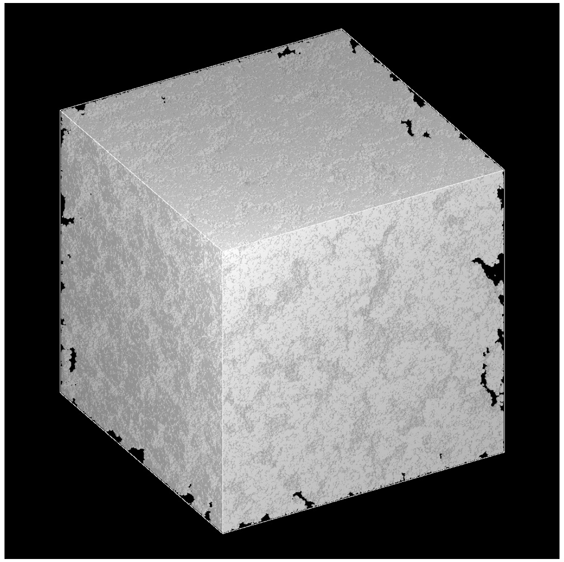
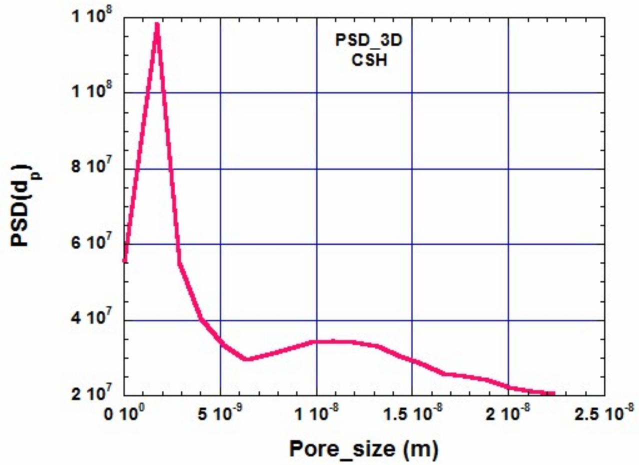
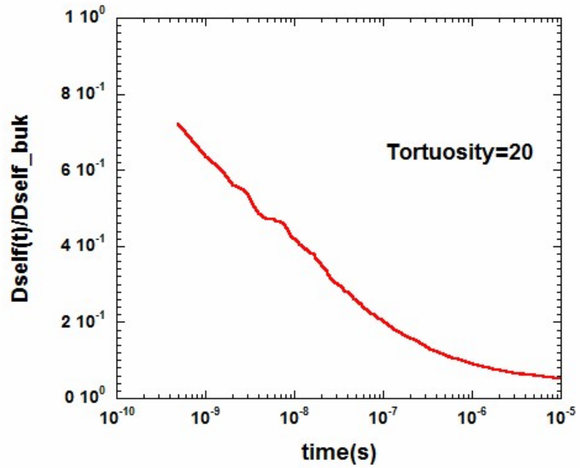


Fig. 3: (a) The C–S–H modulus M as a function of the volume fraction η for our samples and experiments (See Methods and SI). (b) The C–S–H hardness H as a function of the volume fraction η for our samples and experiments (See Methods and SI). (c) Local volume fractions of simulation sample with $\eta = 0.52$ compared with nano-indentation volume fractions of experimental samples S1-S3. (d) Visualization of the spanning network of the densest domains in a sample at $\eta = 0.52$. The particles with $\eta_{local} > 0.66$ are only shown.

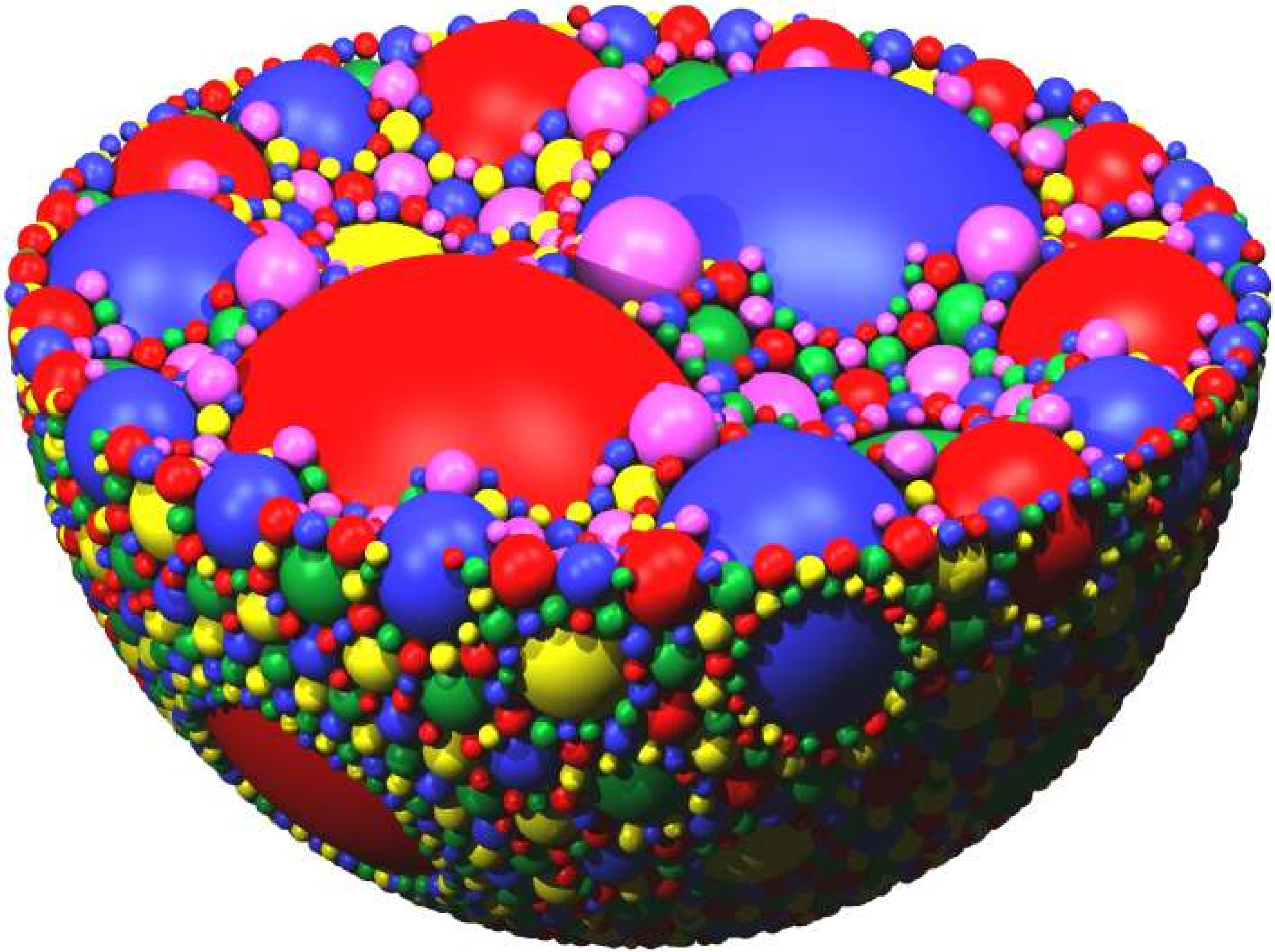



PSD_3D
CSH
PSD(d_p)
1 10^8
1 10^8
8 10^7
6 10^7
4 10^7
2 10^7
0 10^0
5 10^-9
1 10^-8
1.5 10^-8
2 10^-8
2.5 10^-8
Pore_size (m)


Tortuosity=20
Dself(t)/Dself_buk
1 10^0
8 10^-1
6 10^-1
4 10^-1
2 10^-1
0 10^0
10^-10
10^-9
10^-8
10^-7
10^-6
10^-5
time(s)

Conclusion and perspective

- Numerous building porous materials are made of an intricate clustering of polydisperse nanoparticles. The particle organization on a length-scale ranging from nanometers to some micrometers is a cornerstone to properly understand transport properties (diffusion-permeation)
- Imaging techniques at the micro and nano scale are needed for the investigation of the structural evolution of these strongly disordered systems. These experiments have now and in the near future the ability to probe a hierarchical organization on a large length scale ranging from nm to several hundred nm.
- This multimodal structural analysis offers the possibility to use 3D reconstructions and to build constrained models mimicking the geometrical features observed at different length scales. These models can then be used to compute mechanical and transport properties allowing comparison with the experimental determinations.
- Concerning the diffusive molecular transport, we have shown that an intermittent dynamics involving adsorption and relocation inside the pore space can explained a large part of the strong reduction of the water diffusion inside an aged cement paste. The control of the surface "nano wettablity" could then be a way to modify the molecular traffic inside such a complex material on a long period of time..



THANK YOU FOR YOUR ATTENTION !