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  Bio tissues (Bone, Biofilms...)

( CSH grain)  plaster
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 $\mu$m Scale)

$\mu$CT Cement paste during setting (TOMCAT-SLS)
Voxel resolution: 0.7 $\mu$m

Unreacted grains

Hydrated phase

Capillary pore network

We could believe what we see,

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:

\[ C_T = -\frac{(\alpha_{0,I} + \alpha_{0,c} - \alpha_1)}{(\alpha_{0,I} + \alpha_{0,c})} \quad -1 < C_T \]

\[ 0 < C_T \]

**Percolation** \( C_T \approx 0 \)

\[-1 < C_T < 0 \]

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

Microtomographies and their retraction graphs

(Voxel resolution 0.7\(\mu\)m)
Evolution of the capillary pore network

Simulation of the electric transport

F: Formation Factor

\[ F = \frac{R_{\text{Porous -- sample + brine}}}{R_{\text{brine}}} \]

Topological evolution
HOWEVER:

Electric conductivity:
Evaluation of the electric tortuosity at high ionic strength

CEM I, LCPC, 1.5 year old

\[ \text{Tortuosity} = T = \Phi F \]

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

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


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

Tortuosity: \[ T = \frac{D_0}{D} \quad T_r > 20 \]
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 Intermittent Process

\[ D_0 = 2 \times 10^{-9} \text{ m}^2 / \text{s} \]

\[ T(\tau_A = 0) = 2.5 \]

\[ T(\tau_A = 0) = 2.4 \]
The mesoscale texture of C–S–H

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Fig. 3: (a) The C–S–H modulus M as a function of the volume fraction \( \eta \) for our samples and experiments (See Methods and S1). (b) The C–S–H hardness H as a function of the volume fraction \( \eta \) for our samples and experiments (See Methods and S1). (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 \( \text{area} > 0.66 \) are only shown.
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.

Pierre Levitz, CNRS-UPMC, july 2016
THANK YOU FOR YOUR ATTENTION!