EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE · UNIVERSITY OF SURREY

P7: Study of white cement pastes by Nuclear Magnetic Resonance

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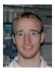
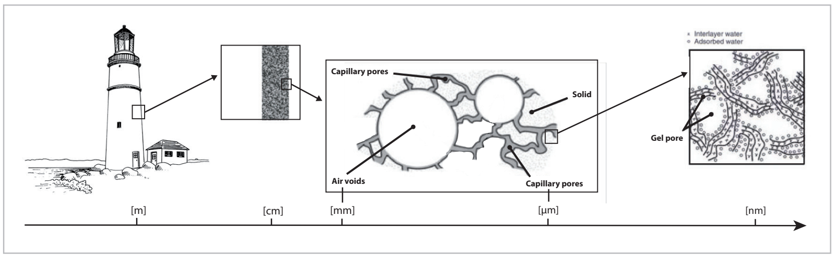


A native of France, Arnaud Muller got his Master degree in civil engineering at University Laval (Québec, Canada). He started to work at EPFL on October 1st 2010.

Project description

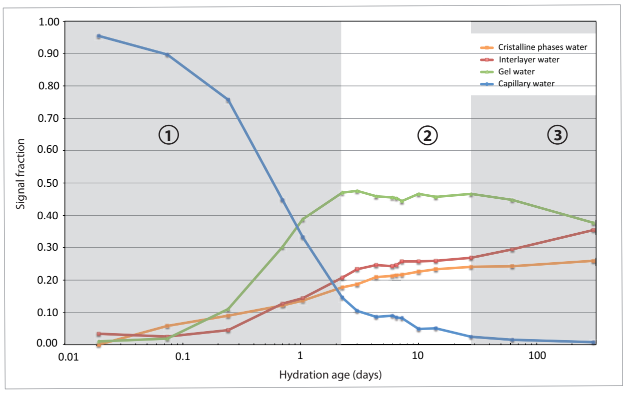
Porosity of cement-based materials forms a complex interconnected network of a wide range of sizes (see right side). Despite numerous studies, there are inconsistencies between authors about size names and ranges when describing pores.

The reasons are twofold. First, C-S-H hydrates, which comprise a significant fraction of the total porosity are difficult to address experimentally due to the nanometric features of their structure. C-S-H morphology as well as its chemical composition are still under debate nowadays. Secondly, most o the different techniques able to assess the pore volume of cement pastes have limitations and often do not measure the whole porosity.



For the past 20 years, ^1H Nuclear Magnetic Resonance (NMR) has been used in order to study the water in cementitious materials. With a resolution of one molecule, the water held in the C-S-H nanostructure can be measured and studied. The aim of this project is to use this new tool to better describe the porosity of cement-based material. The NMR results will act as a basis of comparison with the other «classical» characterisation methods.

Project results



The diagram shows the evolution of the different water signal fractions over the time. There are 3 main stages.

① Portlandite, C-S-H and gel water grow in parallel up to 2 days of hydration.

② After 2 days of hydration, Portlandite and C-S-H continue to grow while the gel water reaches a plateau. This is associated with the formation of a denser C-S-H. In the same time, a slowdown in the consumption of capillary water is observed.

③ When the capillary water has become insignificant (after 28 days), C-S-H layers continue to form using up the gel water, which has become the largest water reservoir.

Calculation model

Mass :

$$1+\frac{w}{c}=(1-\alpha)+\frac{w}{c}\left[\beta I_{solid}+\gamma I_{CSH}+\delta(I_{gel}+I_{cap})\right] \quad \text{(Equ. 1)}$$

Volume :

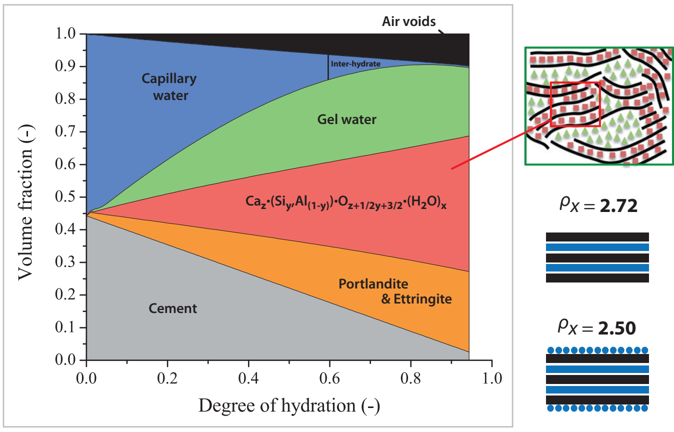
$$\frac{1}{\rho_{uc}}+\frac{w}{c\rho_w}=\frac{(1-\alpha)}{\rho_{uc}}+\frac{w}{c}\left[\frac{\beta I_{solid}}{\rho_{CH}}+\frac{\gamma I_{CSH}}{\rho_{CSH}}+\frac{\delta(I_{gel}+I_{cap}+I_{void})}{\rho_w}\right] \quad \text{(Equ. 2)}$$

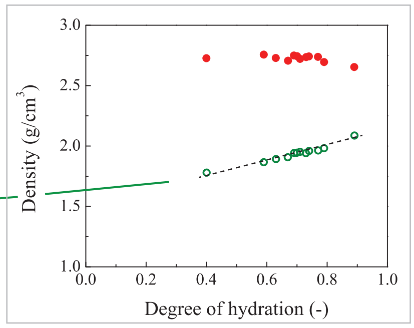
Solving mass and volume balance equations (Equ. 1 and 2), the water signal fractions allow us to fully describe the cement paste at any age.

A phase diagram can be drawn, against for instance the degree of hydration, updating Powers' well known model from 1948.

Our calculation model gives us the chemical equation of C-S-H as written in the diagram. The «solid C-S-H» (excluding of the gel water) exhibits an average equation of
$Ca_{1.7}\cdot(Si_{0.95},Al_{0.05})\cdot O_{3.7}\cdot(H_2O)_{1.8}$
after 7 day of hydration.

Additionally, the C-S-H density can be calculated at any time, including or excluding the gel water. The «bulk C-S-H» density (green dots, right graph) increases over the time as the C-S-H densifies. ρ_{bulk} = 2.09 after 300 days.





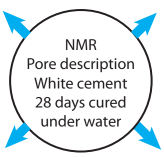
The «solid C-S-H» density (red dots) quicly reaches a plateau in which case ρ_X is about **2.72** ± 0.07. If a surface layer of water is included on the outer surface of C-S-H aggregates, this density drops down to **2.50**.

What I am planning to do for the remaining time

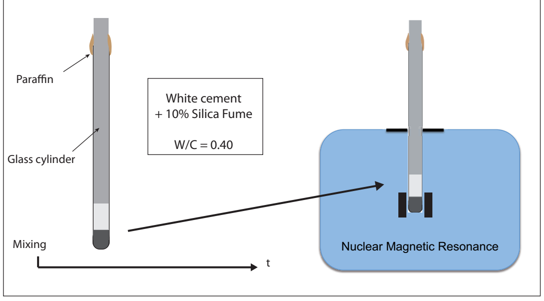
1. Porosity measurement investigation

- Scanning Electron Microscopy (SEM) — Isopropanol exchange, Resin exchange
- Mercury Intrusion Porosimetry (MIP) — Isopropanol exchange
- Water sorption isotherm — No pre-treatment
- Nitrogen sorption isotherm — Isopropanol exchange

NMR
Pore description
White cement
28 days cured
under water



2. Influence of SCMs on C-S-H



3. Impact of different drying methods

NMR
Pore description
White cement
28 days cure-
dunder water

- Oven drying at 50 °C
- Oven drying at 105 °C
- Vacuum drying at 10^{-3} bars
- Vacuum drying at 10^{-6} bars
- Freeze drying
- Solvent exchange (isopropanol and ethanol)

Re-saturation under H_2O → NMR

Outstanding questions

1. What are the best methods to accurately measure the porosity of cement based-material? Where do they fail? Where do they succeed?

2. Have the SCMs an influence on the C-S-H chemical equation and density?

3. How does the drying prior to most of the measurements affect the porosity of a never dried material?

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