Homogenization as a microstructure probe tool
a journey to the interior of cement paste
From concrete nanoscale to structure
celebrating Gilles CHANVILLARD’S memory

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Introduction

Cementitious materials
- have time-dependent properties
- are multi-scale
- host multi-physics processes
- interact with their environment

Homogenization
- can bridge scales: physical processes $\rightarrow$ engineering behaviour
- can estimate microstructure influence on macroscopic properties

But cement paste microstructure
- is difficult to comprehensively observe in its multiscale nature
- may be too complex to be accurately modelled in full details

And cement paste macroscopic properties
- are easy to measure
- are of direct interest for engineers
General strategy

- “focus on first order effects”
  start with a simplified morphological model

- “equations have to be nice and efficient”
  use mean-field homogenization

- “be demanding on model validation”
  compare predictions to experimental measurements

- iterate this trial-and-error process
  - comparison OK ⇒ get other experimental data to compare
  - comparison KO ⇒ go back to morphological model and improve it
Outline

1. Hydrates growing around cement grains
   - Basic morphological model based on MRP
   - Prediction of setting: issues
   - Setting issues: mitigation

2. Introduction of inner/outer hydrates
   - Outer products precipitating as spherical clusters
   - Intermission: does shape matter?
   - Introduction of C-S-H bricks and platelets

3. Further comparisons and extensions
   - Late age: more experimental data
   - Early age: more experimental data and model improvement
   - Towards basic creep: an overview
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**Hydrates growing around cement grains**

**Simplified view of cement paste**

3 phases: **anhydrous, hydrates, capillary porosity**

**A common morphological model**

![Diagram](image)

**Generalized self-consistent scheme**

- **C\text{eff}**
- **C\text{a}**
- **C\text{h}**

heterogeneous solid phase (morphologically representative pattern: layered sphere)

+ **C\text{eff}**

capillary porosity (sphere)
Input data: phases volume fractions and elasticity

Hydration: Powers model [Powers et al., JACI 43, 1946]

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$E$ (GPa)</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>135</td>
<td>nano-indentation$^1$</td>
</tr>
<tr>
<td>0.24</td>
<td>31</td>
<td>nano-indentation$^2$</td>
</tr>
</tbody>
</table>

$^1$[Velez et al., CCR 31, 2001], $^2$[Velez et al., Kurdowski symp., 2001]
Effective stiffness from MRP-based model

$E_{\text{paste}}$ (GPa)

$w/c = 0.3$

$w/c = 0.4$

$w/c = 0.5$

$w/c = 0.6$

Experimental data on cement pastes [Haecker et al., CCR 35, 2005]
Experimental estimation of setting degree of hydration

Experimental data: linear regression [Torrenti et al., MaS 38, 2005], strength data [Byfors, PhD, 1980] and [Taplin, AJAS 10, 1959]
An attempt to interpret SCS implicit morphology

Interpenetrating spheres on primitive cubic lattice

FEM computations $\Rightarrow k_{e f f}$

$\varphi = 0.6$

$\varphi = 0.3$

Self-consistent scheme

$\Rightarrow C_{e f f}$

$C_{e f f}$

solid phase (sphere) + pore space (sphere)
Self-consistent scheme vs spheres on cubic lattice

\[ \frac{k_{\text{eff}}}{k_s} \]

\[ \nu_s = 0.3 \]

\( \varphi \)

SCS

FEM

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Towards a multiscale description

Current morphological model $\approx$ monodisperse distribution of spheres $\Rightarrow$ instantaneous setting for $\frac{w}{c} < 0.32$

To mitigate this issue: **multiscale** description of cement grains starting with two separated scales
Phases volume fractions

**Hydration**: Powers + hydration rate size-independent (simplification)
small particles: 60%

\[
\begin{align*}
\text{w/c } &= 0.3 \\
\text{w/c } &= 0.5 \\
\end{align*}
\]
Effective stiffness from 2-scales MRP-based model

\[ E^{\text{paste}} \text{(GPa)} \]

\( w/c = 0.3 \)
\( w/c = 0.4 \)
\( w/c = 0.5 \)
\( w/c = 0.6 \)

\( \alpha \)

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Setting controlled by outer hydrates

Completely avoid instantaneous setting
consider cement grains as inclusions in a matrix

Introduction of high/low density hydrates as inner/outer products

- High density hydrates (inner)
- Low density hydrates (outer)

Precipitation of hydrate solids (spheres)

Setting of outer $\Rightarrow$ setting of paste
Hydration with HD and LD hydrates

**Hydration:** Powers model

+ repartition HD / LD hydrates [Tennis et al., CCR 30, 2000]

+ $\varphi_{hd} = 0.3$ (from 0.28 [Powers] to 0.30, 0.35 [Tennis et al., CCR 30, 2000])

---

![Diagram showing hydration with HD and LD hydrates]

- $w/c = 0.3$
- $w/c = 0.5$

- LD por.
- LD sol.
- HD por.
- HD sol.
- anh. (anh. = anhydrous)

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Effective stiffness from inner/outer model

\[ E_{\text{paste}} \text{ (GPa)} \]

\[ \alpha \]

\[ w/c = 0.3 \]
\[ w/c = 0.4 \]
\[ w/c = 0.5 \]
\[ w/c = 0.6 \]
Is the spherical shape relevant for hydrate solids?

AFM observation of a $c_3s$ crystal covered by a lime-saturated droplet

[Garrault-Gauffinet, PhD, 1998]

Small particules of C-S-H
anisotropic shape

- parallel to the grain surface
  60 nm by 30 nm
- thickness: 5 nm

⇒ elementary bricks of C-S-H
aspect ratio $r_s = \frac{5}{\sqrt{30} \times 60} \approx 0.12$

Question of the morphology of C-S-H still widely opened
we chose a representation based upon these elementary bricks
The gypsum “interlude”

Gypsum: elongated crystals

Experimental data on gypsum [Meille, PhD, 2001], [Colak, ML 60, 2006], [Ali et al., JMS 10, 1975], [Phani, ACSb 65, 1986], [Tazawa, ACBM 7, 1998]
An attempt to take into account elongated particles

**Elongated particles, random orientation**

Parallelepipeds (21*3*3 voxels) randomly put into a cube

**FEM computations**

Self-consistent scheme

Solid inhomogeneity = prolate spheroid + isotropic orientation distribution

[Meille, PhD, 2001]
Scs with prolate-shaped solid VS FEM

Critical porosity $\varphi^c = 1 - f_s^c$ depends on prolate aspect-ratio $r_s$

FEM results [Meille, PhD, 2001]
**Scs critical solid volume fraction vs geometry**

\[
f_s^c = 1 - \varphi^c
\]

Geometrical percolation of spheroids [Garboczi et al., *PRE* 52, 1995]
Oblate-shaped hydrate solids

- High density hydrates (inner) bricks + gel pores
- Low density hydrates (outer) “platelets” + gel and capillary pores

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### Input data: elastic and morphological parameters

<table>
<thead>
<tr>
<th></th>
<th>$E$ (GPa)</th>
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<th>a.r.</th>
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<td>anh.</td>
<td>135</td>
<td>0.3</td>
<td></td>
<td></td>
<td>nano-indentation$^1$</td>
</tr>
<tr>
<td>hyd. HD</td>
<td>31</td>
<td>0.24</td>
<td>0.3</td>
<td>0.12</td>
<td>nano-indentation$^2$, porosity$^3$, AFM$^4$</td>
</tr>
<tr>
<td>hyd. LD</td>
<td>evol.</td>
<td>evol.</td>
<td>evol.</td>
<td>0.033</td>
<td>self-consistent scheme, hydration model, setting</td>
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<tr>
<td>hyd. solids</td>
<td>71.6</td>
<td>0.27</td>
<td></td>
<td></td>
<td>reverse analysis hyd. HD</td>
</tr>
</tbody>
</table>

LD aspect-ratio: fit on setting results

Rem: atomic scale modelling [Pellenq et al., CCR 38, 2008]

tobermorite C/S=0.83
Young’s modulus: 54 (⊥ sheets); 68, 72 (‖ sheets) GPa

$^1$[Velez et al., CCR 31, 2001], $^2$[Velez et al., Kurdowski symp., 2001], $^3$[Tennis et al., CCR 30, 2000], $^4$[Garrault-Gauffinet, PhD, 1998]
Effective stiffness from inner/outer with bricks/platelets

\[ E_{\text{paste}} \text{(GPa)} \]

\[ w/c = 0.3 \]
\[ w/c = 0.4 \]
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Mature pastes: $\alpha = \alpha_{ult}$

Experimental data [Helmuth et al., Symp. Struct. of Portl. C.P. and Concr., 1966]
Hydration degree at setting

\[ \alpha_{setting} \]

- **MRP**
- **inner/outer spheres**
- **MRP, 2 scales**
- **inner/outer oblates**

**Experimental data** [Torrenti et al., Mas 38, 2005]
Setting: more insights at early age

Continuous monitoring of stiffness, from fluid state?
- **Ultra-sonic meas.** [Boumiz et al., 2\textsuperscript{nd} Rilem workshop on hydration and setting, 1997]
- **EMM-ARM technique** [Azenha et al., CCR 40, 2010]
Scale separation in outer hydrates

- **Hydrates growing around cement grains**
- **Introduction of inner/outer hydrates**
- **Further comparisons and extensions**

**Late age:** more experimental data

**Early age:** more experimental data and model improvement

Towards basic creep: an overview

<table>
<thead>
<tr>
<th>Scale (nm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>bricks</td>
</tr>
<tr>
<td>10</td>
<td>anh. grains</td>
</tr>
<tr>
<td>100</td>
<td>gel pores</td>
</tr>
<tr>
<td>1 µm</td>
<td>capillary pores</td>
</tr>
<tr>
<td>10 µm</td>
<td>outer matrix</td>
</tr>
<tr>
<td>100 µm</td>
<td>LD hydrates clusters</td>
</tr>
<tr>
<td>1 mm</td>
<td>low density hydrates</td>
</tr>
</tbody>
</table>

- **High density hydrates** (inner)
- **Low density hydrates**
- **Small capillary + gel pores**

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Effective stiffness from 2-scales outer

\[ E_{\text{paste}} \text{ (GPa)} \]

- - - - LD pores: monoscale

--- LD pores: small/large

\[ \frac{w}{c} = 0.3 \]
\[ \frac{w}{c} = 0.4 \]
\[ \frac{w}{c} = 0.5 \]
\[ \frac{w}{c} = 0.6 \]

α

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Converting elastic model to basic creep model

Only one extra parameter: Maxwell sliding characteristic time $\tau$
Creep of cement paste vs experimental data

Assumption: frozen microstructure ($\alpha = \alpha^{ult}$)

$\Rightarrow$ Laplace-Carson transform: non-ageing viscoelasticity $\rightarrow$ elasticity

$\varepsilon(t) - \varepsilon_0 \ (10^{-6} / \text{MPa})$

- - - LD pores: monoscale ($\tau = 0.56 \text{d}$)

- - - LD pores: small/large ($\tau = 0.82 \text{d}$)

Experimental data on cement pastes (28 d) [Le Roy, PhD, 1995]
A morphological model of cement paste

- simplified (hydrates not detailed)
- efficient (mean field homogenization)
- validated (at both early and late ages)
- not just about elasticity prediction (can be extended to creep)

Many sources of improvement and prospects

- morphology: differentiate mineral phases + upscale to concrete
- improve chemical modelling
  (hydration, degradation mechanisms, . . .)
- more experimental comparisons
- investigate other mechanical properties
  (creep, strength, damage, . . .)
- investigate transport properties
Paper co-authored with Gilles on cement paste

For more details