Modelling creep and autogenous shrinkage in hydrating cement microstructures

Shashank Bishnoi, Indian Institute of Technology Delhi

With contributions from Quang-Huy Do
Outline

- Microstructural modelling
- Modelling hydration kinetics
- Modelling autogenous shrinkage
  - Modelling porosity
  - Modelling elasticity
  - Modelling creep
  - Modelling shrinkage
Cement microstructure

*SEM image from Vanessa Kocaba
Need of microstructural models

- Cement is a multi-scale material
- It is a complex mix of minerals
- It is a less understood material
- It is mixed with other even lesser understood materials
- It is studied using indirect techniques
- It is not always possible to explain its behaviour using analytical equations
We need numerical models

- We need numerical models to
  - To account for the large number of factors
  - To help analyse and design experiments
  - To test hypotheses
  - To make predictions possible
  - To bring some order to the disorder!
Requirements from a model

- To account for the large number of factors and scales:
  - Multi-scale and Powerful

- To account for the unknown:
  - Flexible and Extensible

- To encourage its use:
  - Easily accessible, Fast and User-Friendly
\(\mu ic\) modelling platform

- \(\mu ic\) stands for Microstructure
- \(\mu ic\) is a modelling platform that enables vector modelling of cement microstructure
- \(\mu ic\) enables studying hypothesis
- \(\mu ic\) models particulate reactions
- Local physics and chemistry input to \(\mu ic\) as models
- Microstructural and global effects of local rules calculated
The idea

Cement $\rightarrow$ Hydrate 1 + Hyd 2

Kinetics

Compensate for overlaps
Advantage of vector approach

- Much higher resolution possible
- Possible to represent features of wide size range

<table>
<thead>
<tr>
<th>ld</th>
<th>r</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.2</td>
<td>14.76</td>
<td>85.62</td>
<td>73.6</td>
</tr>
<tr>
<td>1</td>
<td>5.6</td>
<td>59.12</td>
<td>85.6</td>
<td>61.78</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>86.99</td>
<td>39.7</td>
<td>44.98</td>
</tr>
</tbody>
</table>
\( \mu \text{ic has no hard-wired information} \)
Flexibility: materials and particles

- Inner C-S-H
- Outer C-S-H
- Alite + Belite
- CH
- Silica Fume
- C-S-H
Flexibility: mechanisms

Variants

\( x\% \) on reacting particle
\( y\% \) in pores
\( z\% \) on filler particles

or

Deposit in proportion of area available on reactive and filler particles
Many types of microstructures can be produced and analysed...
Versatility of $\mu$ic

Nucleation of single material
Versatility of \( \mu\text{ic} \)

Surface growths
Versatility of μic

Fibrous growths
Reaction kinetics

\[ \text{Fraction}_{\text{fill}} = 1 - e^{-kt^n} \]
Hydrating cement microstructure
Setting
Versatility of $\mu$ic

Many materials and hollow shells
Phase fractions
Versatility of $\mu$ic

Cements with fine fillers
Pore-size distributions

![Graph showing pore-size distributions for different cement compositions]

- **C₃S**
- **C₃S with 10% replacement**
- **C₃S with 5% replacement**
- **C₃S with 10% replacement without C-S-H deposition**
- **C₃S with 5% replacement with large filler**

Volume of pores (% of total volume larger than)

Pore Diameter (μm)
Versatility of $\mu$ic

Mortars fine cements and ITZ
Effective w/c due to ITZ

![Graph showing normalized w/c against distance (micro metres)].

- Blue line: 0.3 w/c
- Red line: 0.4 w/c
- Yellow line: 0.5 w/c
Modelling autogenous shrinkage using $\mu$ic
Autogeneous shrinkage: introduction

\[ V_{\text{product}} < V_{\text{water hydrated}} + V_{\text{cement hydrated}} \]

(Le Châtelier 1900)

- After setting, decrease in total volume, accommodated by formation of voids, auto-desiccation, contraction of solid due to force induced by water menisci

- This may lead to cracking

- Autogeneous shrinkage is difficult to predict

- This thesis uses a numerical approach based on mechanisms using accepted values of properties of phases without fitting
Modelling approach

This approach aims to directly link microstructure and autogeneous shrinkage based on the capillary tension mechanism.
Homogenization based on FEM

Assumption in this simulation:

- Every element is homogenous
- All phases: isotropic, elastic, from nano-indentation
- Perfect bonds between solids
- Saturated pores, water flow and pore pressure neglected
Homogenization based on FEM

- Homogeneous boundary conditions (force and displacement)
- Uniform mesh with linear elements

\[ K \{d\} = \{F\} \]

stiffness \hspace{2cm} displacement \hspace{2cm} applied force

\[ \varepsilon = \frac{1}{V} \int \varepsilon \, dV \]

\[ \sigma = \frac{1}{V} \int \sigma \, dV \]

\[ \sigma = C \varepsilon \]

\[ C = \frac{E}{(1 + \nu)(1 - 2\nu)} \begin{bmatrix} 1 - \nu & \nu & \nu & 0 & 0 & 0 \\ \nu & 1 - \nu & \nu & 0 & 0 & 0 \\ \nu & \nu & 1 - \nu & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1 - 2\nu}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1 - 2\nu}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1 - 2\nu}{2} \end{bmatrix} \]
Artificial connections may be induced due to meshing when distances are smaller than mesh size.
Two burning algorithms

“Global burning” works at computational volume level:

To remove all clusters that are not connected to the faces (where the boundary condition are applied) of the computational volume

“Local burning” works at voxel level:

To verify that a “solid” connection exists between two faces of a voxel

Before “burning”  After “burning”  Burning in one voxel
Effect of burning algorithms

Data from Boumiz 1996

"Double burning" provides results in good agreement with experiment
Simulations capture effect of w/c

Data from Boumiz 1996
Flocculation for initial packing of particle in a system

Flocculation makes average distance between closest particles in the system to be smaller

The distance of particles 1 and 2 is halved
Flocculation for initial packing of particle in a system

Flocculation makes average distance between closest particles in the system to be smaller
Simulation with flocculation can capture percolation.
C-S-H densification can capture percolation

Data from Boumiz 1996

Physically plausible explanation of percolation
Modelling creep using μic
**Basic ageing creep simulation by FEM**

In this simulation:

- **Only C-S-H is viscoelastic**
- **Everything else like in elastic modelling**

The development of microstructure is updated during creep simulation.
Intrinsic C-S-H viscoelasticity from nano-indentation

Contact creep compliance (Vandamme 2008):

\[ L(t - t_0, t_0) = \frac{1}{M} + \frac{1}{C} \ln \left[1 + \frac{t - t_0}{\tau}\right] \]

- **M**: Elastic indentation modulus
- **C**: Contact creep modulus
- **τ**: Characteristic viscous time (1.66 s)

\( C = 1.355M^{1.41} \)

\( = 1588.9(\eta - 0.5)^{1.597} \)

- Constant C-S-H density of 2 g/cc
- C-S-H densification (0-2 g/cc)
Intrinsic C-S-H creep compliance is fit by Maxwell chain

\[ J \text{ (microstrain/MPa)} \]

\[ \text{Time (hour)} \]

\[ \text{Density assumed } = 2.0 \]

\[ \text{Nano-indentation experiment } \quad \diamond \quad \text{Numerical fitting} \]

<table>
<thead>
<tr>
<th>Young's modulus $E$ [MPa]</th>
<th>7629</th>
<th>5548</th>
<th>3773</th>
<th>1526</th>
<th>1526</th>
<th>5548</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\sum E_i = 25550$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relaxation time $\tau_i$ [hour]</td>
<td>0.001</td>
<td>0.01</td>
<td>0.7</td>
<td>40</td>
<td>700</td>
<td>$+\infty$</td>
</tr>
</tbody>
</table>
Ageing intrinsic C-S-H creep compliance

\[ J(\tau) = \frac{1}{E} + \frac{1}{C_{\text{uniaxial}}} \ln \left[ 1 + \frac{t-t_i}{\tau} \right] \]

For a simulation at loading at \( t_0 \), multi-compliances are needed due to densification

E.g. 4 particles of C-S-H formed at \( t_0, t_1, t_2 \) and \( t_3 \)
Creep results with constant C-S-H density = 2.0 g/cc

loading at 18, 24, 30 hours

Data from Tamtsia et al. 2004 (w/c 0.5)
Creep results with C-S-H densification

Data from Tamtsia et al. 2004

loading at 18, 24, 30 hours

Experiment
Simulation with density 2.0
Simulation with densification

Data from Tamtsia et al. 2004 (w/c 0.5)
Modelling pore structure using μic
Pore structure simulation based on "voxel erosion"

Pores are the space not filled by solids: very complex shape

Previously computation problem to approach nm resolution to represent capillary pores down to 10 nm or less

In this work:

- Improve algorithm from Bishnoi (CCR 2009) – speed x10
- Parallelize pore size simulation (simulation at 5 nm resolution takes 1 day)
- Develop MIP simulation algorithm (not possible with parallelization)
Pore structure simulation based on "voxel erosion"

**Pore Size Simulation:**
Characterization of pore sizes ignoring pore connectivity

Identify pore domains by “walk back” to solid boundaries

Pore size (voxel)  Solid
MIP simulation

But no experimental method to determine real pore size distribution

Best quantitative technique for capillary porosity is MIP, which measures pore entry

Mercury flows from the surfaces of microstructure

Pore size (voxel) 1 2 3 4
Solid
2 simulation approaches to analyse pore structure

3D-Simulation based on voxel erosion

✓ Pore Size Simulation
Characterization of pore sizes ignoring pore connectivity

Pore size (voxel) 1 2 3 4 5
Solid

✓ MIP Simulation
Pore sizes have sizes as their access diameters from surfaces taking into account pore connectivity and the pore-entry-effect
Simulations to compare with measured data from Chen

Initially assumed constant density for C-S-H of 2.0 g/cc

Total porosity is higher compared with that from MIP experiment
Simulations compared to data from Chen

Calibrating total porosity with MIP experiment

\[ \rho(t) = 2.0 - (\exp(-0.207t) + \exp(-0.054t)) \]

<table>
<thead>
<tr>
<th>Density</th>
<th>DoH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>8%</td>
</tr>
<tr>
<td>1.38</td>
<td>23%</td>
</tr>
<tr>
<td>1.97</td>
<td>60%</td>
</tr>
</tbody>
</table>

8% DoH

23% DoH

60% DoH
Calculated densities compared to NMR measured

Bulk density (g/cc) vs. Degree of Hydration (-)

Data from NRM (Muller et al. 2012) ▲ Results from this study
Simulations to compare with measured data from Chen

Large divergences between simulation and experiment

Need to improve simulations by test of numerical parameters

<table>
<thead>
<tr>
<th>Density</th>
<th>DoH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>8%</td>
</tr>
<tr>
<td>1.38</td>
<td>23%</td>
</tr>
<tr>
<td>1.97</td>
<td>60%</td>
</tr>
</tbody>
</table>

8% DoH

23% DoH

60% DoH
Effects of parameters on simulation results

Effect of resolution

- 200 nm resolution
- 100 nm resolution
- 10 nm resolution
- 5 nm resolution

Fraction larger than (-)

Radius (micron)

74% DoH
Effects of parameters on simulation results

Effect of number of new CH nuclei
(high nuclei with 400,000 grains against 5,000)

![Graph showing the effect of number of new CH nuclei on pore size distribution. The graph compares the fraction of pores larger than a certain radius in micron, with lines representing different conditions: Reference, More nuclei, MIP - Reference, and MIP - More nuclei. The graph indicates a 74% DoH.]
Effects of parameters on simulation results

Effect of particle shape

- Pore size - Reference
- Pore size - Cylinders
- MIP - Reference
- MIP - Cylinders

Microstructure is converted from spheres to cylinders

74% DoH
Effects of simulation parameters: “roughening”

25 % probability of conversion:
- pore-voxels $\rightarrow$ solid-voxels and the same number
- solid-voxels $\rightarrow$ pore-voxels

Reference (original)  5 steps roughening  10 steps roughening
Effects of simulation parameters: “roughening”

MIP measured breakthrough

Rougher microstructures appear to have finer pore sizes and the breakthrough diameter shifts closer to the measured one.

Estimate that roughening extends into pore space at least 90% of pore size.
After 2 days, only inter-hydrate pores

Data from NMR (Müller 2012)
“Nature of C-S-H”

C-S-H grows, like needles, in a very diffuse manner in pore space.

35% DoH, simulation 10 steps roughening

Real sample 25 hours by TEM (Bazzoni LMC)
Modeling flowchart of autogenous shrinkage

Hydration model μic

Porosity

Mechanical (Elasticity & creep)

Capillary pressure

Creep-superposition method

Poro-elastic method

Autogeneous shrinkage

Relative humidity test

MIP test & chemical shrinkage
Simulation for Portland cement

Results of Young ‘s modulus

Results of Poisson ‘s ratio

Data from Chen 2011

S. Bishnoi, IIT Delhi
Measured RH and calculated RH from CS & MIP
Capillary stress calculated from RH

\[ p_c = \frac{RT \ln (RH)}{V_m} = \frac{RT \rho \ln (RH)}{M_m} \]

Before 24 hours relative humidity was calculated from MIP and chemical shrinkage experiments

Data from Chen 2012
Modelling based on poro-elastic method

Homogenization based Self-Consistent scheme:

\[ \varepsilon_{\text{LIN}} = \frac{S \sigma_{\text{cap}}}{3} \left( \frac{1}{K} - \frac{1}{K_s} \right) \] (Mackenzie 1950)

- \( S \): degree of saturation (according to Powers’ model 1965)
- \( \sigma_{\text{cap}} \): capillary stress
- \( K \): bulk modulus of cement paste
- \( K_s \): bulk modulus of solid (= 44 GPa, Nielsen 1991)

Data from Chen 2012
Modelling based on poro-elastic method

Data from Chen
2012
Boltzmann creep-superposition method

\[ \varepsilon(t) = \int_{t_0}^{t} J(t, t') d\sigma(t') \quad \text{where} \quad \sigma(t') = (1 - 2v) p_c \phi \quad \text{(Force contributes to volumetric strain)} \]

\[ \varepsilon(t) = J(t, t_0)\sigma_0 + J(t-t_1,t_1)\Delta\sigma(t_1) + J(t-t_2,t_2)\Delta\sigma(t_2) + J(t-t_3,t_3)\Delta\sigma(t_3) + \ldots \]

**Deformation calculated using:**

Decomposition of history of volumetric capillary stress into differential terms and their corresponding creep compliance (plotted in the same colours)
Modelling based on creep-superposition method

Data from Chen 2012
Summary

- Microstructural modelling
- Modelling autogenous shrinkage
  - Modelling mechanical properties
  - Modelling porosity
  - Modelling shrinkage
- Practical applications
Thank you!