MICROMECHANICS OF HYDRATING CEMENT PASTES
considering C-S-H gel densification

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Introduction

Microstructure of cement paste

Cement paste is a hierarchically organized **heterogeneous material**. The chemical reaction between cement clinker and water produces several types of **hydration products**, including most importantly **calcium silicate hydrates (C-S-H)**. Remaining water fills capillary pores and **gel pores**, whereby the latter are smaller. Gel pores together with solid C-S-H crystals form the so-called **C-S-H gel**, the binding phase of all concretes.

C-S-H densification and hydration modeling

While classical hydration models (e.g. the widely used Powers model [1]) predict constant gel porosities, recent nuclear magnetic resonance (NMR) measurements [2] revealed that the **C-S-H gel densifies** during the hydration. By relating the C-S-H gel density to the **space confinement** for precipitating C-S-H crystals, the NMR-measured densification behavior can be predicted. Quantification of this confinement is done by introducing a pore space within the volume of cement paste, which is available to host precipitates - or in

short, the specific precipitation space γ. This opens the door to predict the volume evolutions (as function of the degree of hydration ξ) of all constituents of cement paste of any cement composition (expressed by the water-to-cement mass ratio w/c), which is a prerequisite for our continuum micromechanical models.

Micromechanics approach for poroelastic upscaling

The heterogeneous microstructure of cement paste is resolved on **three observation scales**, starting at nanometer scale with the C-S-H gel. At this scale, **C-S-H crystals** are considered to precipitate with shapes depending on the available precipitation space γ. At the micrometer scale, C-S-H gel needles are intermixed with capillary pores and air voids, and on the millimeter scale portlandite plates and clinker grains are considered. This multiscale approach allows us to upscale the stiffness of the nanometer-sized solid C-S-H particles, which stems from atomistic models [3], to the macroscopic stiffness of cement paste. Experimental validation corroborates the predictive capabilities of the model. Our poromicromechanics approach also quantifies the **stiffening effect of water** in gel and capillary pores.

Poroelastic multiscale model

Multiscale microstructural representation

Based on the separation of scales principle [4], representative volume elements (RVEs) are resolved on three scales of observations:

(a) cement paste — 1 mm — clinker, CH plates, hydrate foam matrix
(b) C-S-H foam — 1 µm — air voids, capillary pores (water-filled), C-S-H gel elements
(c) C-S-H gel — < 50 nm — solid C-S-H crystals, gel pores (water-filled)

Poroelastic homogenization

Stepwise: C-S-H gel (self consistent) → C-S-H foam (self consistent) → cement paste (Mori-Tanaka)

Drained:
- pore space unsealed, all pore pressures vanish $p_{gpor} = 0$, $p_{cpor} = 0$
- homogenization based on continuum micromechanics [4]:

$$\mathbb{C}_{hom}^{drained} = \sum_{i=1}^{n} f_i \, \mathbb{C}_i : \mathbb{A}_i$$

Homogenized stiffness tensor | phase volume fraction | phase stiffness | phase strain concentration tensor (from Eshelby-type Matrix-Inclusion problems)

- behavior expected to be observed under "slow" mechanical testing

Undrained:
- pore space fully water-saturated and sealed $p_{gpor} > 0$, $p_{cpor} > 0$
- homogenization based on eigenstress influence tensor concept [5]

$$\mathbb{C}_{hom}^{undrained} = \mathbb{C}_{hom}^{drained} + \int_0^{2\pi}\int_0^\pi \boldsymbol{B}_{gpor} \otimes \boldsymbol{L}_{gpor} \frac{\sin\vartheta}{4\pi} d\vartheta d\varphi + \boldsymbol{B}_{cpor} \otimes \boldsymbol{L}_{cpor}$$

stiffening effect of capillary pores | gel pore pressures depend on the orientation of C-S-H gel needles | stiffening effect of capillary pores

- behavior expected to be observed under "fast" ultrasonic test / resonance tests

Hydration model considering C-S-H gel densification

Our approach rests on the hypothesis that **space confinement** of precipitating C-S-H crystals **drives the densification of the C-S-H gel**. Space confinement is quantified by the porosity of the hydrate foam denoted as **specific precipitation space** γ:

$$\gamma = \frac{V_{gpor}+V_{cpor}}{V_{sCSH}+V_{gpor}+V_{cpor}}$$

V_{gpor} ... gel pore volume
V_{cpor} ... capillary pore volume
V_{sCSH} ... solid C-S-H volume
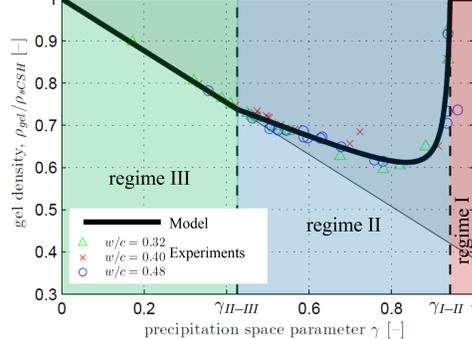
To study the C-S-H gel density ρ_{gel}, **three hydration regimes** are envisioned:

I C-S-H crystals precipitate in **ordered** fashion on clinker surfaces **without entrapping gel pores**:
$\rho_{gel} = \rho_{sCSH}$

II C-S-H crystals grow in a **less ordered** fashion such that **gel pores are enclosed**. This new class of hydrates densify linearly with decreasing precipitation space.

III once all capillary pores are filled, solid C-S-H crystals precipitate inside the gel porosity:
$\rho_{gel} = \rho_{sCSH}(1-\gamma) + \rho_{H_2O}\,\gamma$

C-S-H gel densities and stoichiometric/kinetic relations for the hydration of typical Portland cement (consisting of 70% alite and 30% belite) allow for calculating **phase volumes fractions** of clinker, CH, solid C-S-H, gel pores, capillary pores, and air voids as functions of the hydration degree and the water-to-cement mass ratio. Hydration stops either if all clinker or all water is consumed, expressed by the ultimate hydration degree ξ_{ult}, however, in regime III hydration is expected to slow down dramatically.

Input Properties

- Clinker: spherical shape, stiffness from nanoindentation experiments [6]
- Solid C-S-H: precipitation space drives the shape (plate-shape at $\gamma = 0$, spherical shape at $\gamma = 1$), stiffness from atomistic modeling [3], chemical composition and density from SANS/SAXS [7]
- Portlandite: plate-shaped, stiffness from Brillouin spectroscopy experiments [8]
- Pores/voids: spherical shape, linear compressive behavior of water

Results and discussions

Validation: hydration model

The work of Muller et. al. [2] also provides a possibility to check our model-predicted phase volume fractions. They combined NMR, Rietveld analyses of X-ray diffraction patterns, thermal gravimetric analysis, and chemical shrinkage measurements, for identification of phase volume evolutions.

colored areas ... experiments
Black lines ... model predictions
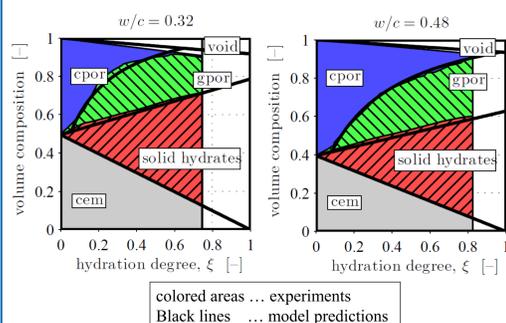
✓ accounts for nonlinear evolution of gel porosity
✓ nicely predicts the transition hydration degree where capillary pores vanish

The model is valid for plain Portland cement paste (and white cement paste), hydrated at room temperature under sealed conditions.

Validation: poroelastic model
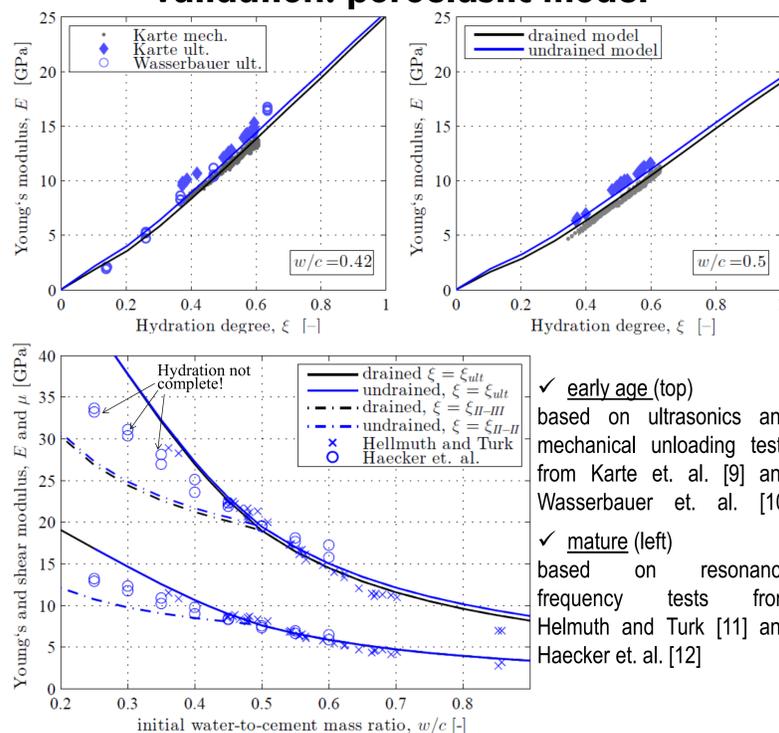
✓ **early age** (top)
based on ultrasonics and mechanical unloading tests from Karte et. al. [9] and Wasserbauer et. al. [10]

✓ **mature** (left)
based on resonance frequency tests from Helmuth and Turk [11] and Haecker et. al. [12]

Stiffening effect of water
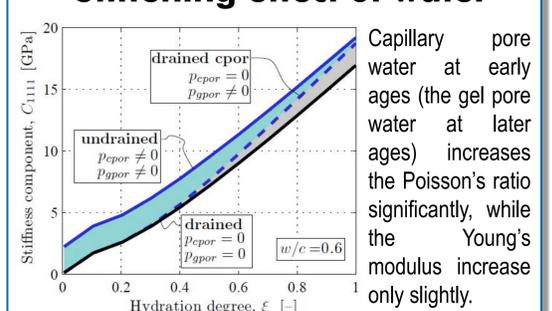
Capillary pore water at early ages (the gel pore water at later ages) increases the Poisson's ratio significantly, while the Young's modulus increase only slightly.

Conclusions

- **Space confinement** in the precipitation space **drives** the **densification of C-S-H gel**
- from solid C-S-H stiffness obtained in atomistic models, the macroscopic poroelastic response of cement paste can be predicted very accurately → **molecular-to-continuum scale bridging**

Outlook

- **Extending the** mechanical model in order to predict the **viscoelastic behavior**
- Quantifying microstructural **stress concentrations** allows for **strength** predictions

Contact

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Publications

- Königsberger, Pichler, Hellmich. *Densification of cement hydration products is mainly driven by available precipitation space - arguments from a new mathematical model integrating data from NMR experiments*. In preparation.
- Königsberger, Pichler, Hellmich. *Molecular-to-continuum poroelasticity upscaling of hydrating cement pastes considering progressive C-S-H gel densification*. In preparation.