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Modeling the apparent and intrinsic viscoelastic relaxation of hydrating cement paste

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ABSTRACT

Finite element procedures combined with microstructure development modeling are integrated to quantitatively predict the viscoelastic/viscoplastic relaxation of cement paste due to intrinsic calcium silicate hydrate viscoelasticity and microstructure evolution associated with the hydration process. The combined models are implemented in a computational routine to predict time-dependent stress and strain fields in cement paste. The model simulations suggest that inherent viscoelastic deformation caused by calcium silicate hydrate is not necessarily the primary mechanism leading to the overall early-age viscoelastic/viscoplastic behavior of cement paste. The effect of time-dependent dissolution of cement grains occurring during the hydration process is substantial and should be considered as a significant mechanism for the apparent viscoelasticity/viscoplasticity of cement paste.

1. Introduction

Previously, a model implementing the finite element method (FEM) was used to successfully predict the elastic properties of cement paste based on the elastic properties of the microscopic phases and their evolving spatial structure [1]. However, it is widely known that cement paste exhibits viscoelastic/viscoplastic (VE/VP) effects in addition to the instantaneous elastic effects; such time-dependent VE/VP effects have a significant impact on the stress and strain fields in cementitious materials [2]. Theoretically predicting the VE/VP relaxation moduli of cement paste is a difficult task. In addition to its complex, random, composite matrix arrangement at the micrometer scale, the microstructure evolution of cement paste during the hydration process is an additional important complexity, as its response to load critically depends on loading histories relative to the time the new components are formed.

The VE/VP behavior of cement paste has been traditionally attributed to the inherent VE/VP behavior of the calcium silicate hydrate (C-S-H) phase [2], and based on this understanding, many mechanisms towards C-S-H VE/VP behavior have been proposed, such as the seepage theory [3,4] and the viscous shear theory [3,5]. Besides inherent C-S-H VE/VP effects, researchers have also suggested other mechanisms leading to time-dependent deformation of cement paste, including poromechanical effects (see, e.g., [6–11]) and dissolution of load bearing phases [12,13]. Poromechanical effects manifest as a time-dependent transfer of stress from the pore fluid phase to the solid skeleton inside saturated cementitious materials, which leads to an effective relaxation of the moduli [14,15]. Similarly, an effective relaxation of the moduli, shown in preliminary results of the model described in this present paper, may also occur due to the redistribution of stress generated by the dissolution of load bearing solid phases [16]. Since the effect of poromechanics is apparently only substantial when the material is fully saturated, in this paper, the main VE/VP mechanisms considered are the intrinsic VE/VP behavior of C-S-H and the time-dependent dissolution of cement grains. While it is well known that drying of cementitious materials while under load enhances deformation (i.e., the so-called "drying creep" or "Pickett effect"), the consideration of drying is outside the scope of the present paper and thus will not be addressed.

The objective of this research is to develop a model using computational methods to predict the evolution of VE/VP properties of hydrating cement paste based on the aforementioned mechanisms. By carrying out virtual experiments using the model, the contribution of each mechanism towards the overall VE/VP behavior of cementitious materials can be evaluated.

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2. Methodology and model validation

2.1. Microstructure modeling

The previously referenced prediction of cement paste elastic moduli involved utilizing the microstructure model CEMHYD3D (CEMent HYDration in 3D) [17], which generated lattice-based 3D digital microstructure images of specific cement pastes at specific degrees of hydration. Each voxel in the 3D microstructure was treated as an eight-node tri-linear cubic element in a finite element solver at the micrometer scale. By assigning individual phase elastic moduli to each voxel (depending on which individual phase occupied each voxel) and applying periodic displacement boundary conditions, the finite element program predicted the full 3D stress and strain fields [1,18,19]. These fields were spatially averaged over the microstructure to determine the composite elastic moduli at a given degree of hydration and then compared to experiments where both elastic moduli and degree of hydration were measured [20].

In the computational approach undertaken in this research, a next-generation hydration model called THAMES (Thermodynamic Hydration And Microstructure Evolution) [21,22] was utilized to simulate the microstructure evolution during the hydration process at the micrometer level. THAMES is capable of producing 3D snapshots of hydrating cement paste microstructure at different ages based in part on thermodynamic equilibrium calculations and phenomenological dissolution kinetics [21]. The input provided to THAMES was the phase makeup (mass fractions of constituents) of the cement considered at the particle level, the particle size distribution of the cement, and the water to cement ratio (w/c). THAMES randomly placed the digital cement grains within a specified domain, and the grains began to dissolve at the surface according to phenomenological dissolution kinetics functions. At each time step, the pore fluid speciation from the previous time step was combined with the change in speciation induced from dissolution since the previous step. Based on the new speciation at the present time step, the thermodynamic engine GEMS (Gibbs Energy Minimization) [23,24] was utilized to find the equilibrium solution speciation and the mass of each solid constituent in equilibrium with the solution. It was assumed that near-equilibrium conditions were present between the hydration products and pore solution, which is a reasonable approximation after about 12–24 h of hydration for typical portland cement pastes. The new hydration products formed at a particular time step were spatially located based on local geometric information regarding interfaces. This information included restrictions on where a particular constituent can grow and empirical information regarding the growth habit of the constituent (i.e. random, acicular, isotropic). The output from THAMES at each time step is a representative microstructure of constituents, in which each cubic voxel consists of a single phase.

2.2. Finite element method

Finite element procedures were rewritten in C++, based on the existing Fortran codes [18,19], to match THAMES, since it is also written in C++. The finite element codes were combined with the THAMES microstructure model to develop an elastic moduli prediction model as well as a VE/VP relaxation moduli prediction model. In each case, the THAMES microstructure was meshed using a spatially aligned numerical discretization [25] such that each voxel (consisting of a unique phase) became an eight node tri-linear cubic finite element. In the elastic properties prediction model, each voxel was assigned isotropic elastic moduli. For anisotropic crystalline phases, the effective average isotropic moduli were calculated as the arithmetic average of the Voigt and Reuss polycrystalline bounds [26]. This procedure was deemed an accurate approximation owing to the probable random orientation of these phases within a given microstructure. The microstructure was subjected to strain-controlled periodic displacement boundary conditions and the total mechanical energy stored inside the whole microstructure was minimized to solve the boundary value problem [1,19]. The composite elastic moduli were calculated by solving the elastic equations on a regular finite element mesh [20], based on the volume averaged stress of the composite under the specific boundary condition. A similar approach has yielded elastic moduli that agree well with the experimental results obtained from general porous materials and also cement paste specimens fabricated using the same cement and w/c considered in the simulations [1,27].

To predict the time-dependent VE/VP behavior of cement paste, the elastic microstructure model was discretized in time to account for the time and (stress or strain) history dependent mechanical properties. At each time step in the finite element calculations, the microstructure model THAMES provided a snapshot of the 3D time-evolving microstructure, and similarly to the elastic moduli prediction model, the VE/VP finite element model solved the strain-controlled viscoelastic problem by minimizing the total energy stored in the microstructure at each time step.[1] The virtual work principle was used with the viscoelastic model to calculate the mechanical energy of the viscoelastic phases inside the microstructure [28,29].

In the domain Ω of the problem, the virtual work expression for stored mechanical energy is derived under a virtual stress boundary condition induced by the traction condition

$$t_i = \sigma_{ji} n_j \tag{1}$$

for all points lying on a part of the boundary denoted as S_2, where are components of the Cauchy stress tensor and n_j are components of the unit normal vector [30,31]. A variational form of virtual work for infinitesimal deformations is

$$\int_\Omega \delta u_i b_i d\Omega + \int_{S_2} \delta u_i t_i d\Omega - \int_\Omega \delta u_i \rho \ddot{u}_i d\Omega - \int_\Omega \delta\varepsilon_{ij}\sigma_{ij} d\Omega = 0, \tag{2}$$

where ρ is mass density, b_i are body force components, u_i are displacement components, ε_{ij} are infinitesimal strain components, δ denotes an infinitesimal variation, and the overhead dots denote partial differentiation with respect to time [29]. Under a quasi-static state with a negligible inertia, the terms containing velocity components in Eq. (2) can be eliminated and the instantaneous stored energy in viscoelastic phases can be approximated as

$$\psi = \frac{1}{2}\int_\Omega \varepsilon_{ij} C_{ijkl} \varepsilon_{kl} d\Omega + \int_\Omega u_i b_i d\Omega, \tag{3}$$

where ψ is the energy stored in viscoelastic phases and C_{ijkl} are components of instantaneous elastic moduli. Through minimizing the total mechanical energy stored in the microstructures, stress and strain fields of these microstructures at each time step can be predicted through FEM. While cementitious materials are rarely subjected to large deformation gradients on the macroscopic length scale – owing to their quasi-brittle nature – it is possible that locally large deformation gradients might still occur in the microstructure. While infinitesimal strains are considered in the analysis discussed herein, further study is needed to determine the likelihood of finite strains in the microstructure.

Prescribed, periodic volumetric strain and prescribed, periodic shear strain were applied on the boundaries of a series of

[1] This solution procedure for the VE/VP material problem disregards any linear momentum in the body associated with its motion. This approach generates negligible error since the velocity of the time-dependent deformation is extremely slow under the boundary conditions considered.