# 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.

Keywords: C-S-H [B]; Finite Element Analysis [C]; Microstructure [B]; Viscoelastic; Dissolution; THAMES

## 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.

### 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 hrs 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.<sup>1</sup> 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  $\Omega$  of the problem, the virtual work expression for stored mechanical energy is derived under a virtual stress boundary condition induced by the traction condition

<sup>&</sup>lt;sup>1</sup> 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.

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

for all points lying on a part of the boundary denoted as  $S_2$ , where  $\sigma_{ij}$  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

$$\int_{\Omega} \delta u_i b_i d\Omega + \int_{S_2} \delta u_i t_i d\Omega - \int_{\Omega} \delta u_i \rho \ddot{u_i} d\Omega - \int_{\Omega} \delta \varepsilon_{ij} \sigma_{ij} d\Omega = 0, \qquad (2)$$

where  $\rho$  is mass density,  $b_i$  are body force components,  $u_i$  are displacement components,  $\varepsilon_{ij}$  are infinitesimal strain components,  $\delta$  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

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

where  $\psi$  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.

**Fig. 1** Conceptual diagram of model simulating apparent VE/VP behavior of hydrating cement paste due to microstructure evolution, where  $\sigma$  is an applied external macroscale stress and t is time elapsed. (a) Before application of load, there exists a certain amount of unhydrated phases. (b) Load is applied and existing components deform due to elastic mechanical properties. (c) Hydration occurs and some unhydrated load bearing cement grains dissolve, increasing the stress in surrounding phases. Stress and strain redistributes to maintain the boundary condition and the overall deformation field of the composite microstructure changes. Even if nearby phases are purely elastic, the overall change of deformation depends on when dissolution occurs, resulting in apparent VE/VP behavior. (d) New components form in the deformed configuration with apparent strain and zero stress.

Prescribed, periodic volumetric strain and prescribed, periodic shear strain were applied on the boundaries of a series of microstructures at different ages to determine the evolutions of cement paste VE/VP bulk modulus and VE/VP shear modulus. The expressions were subjected to Laplace transformations to determine the VE/VP Young's modulus and Poisson's ratio from the VE/VP bulk and shear moduli. The resultant VE/VP Young's modulus and VE/VP Poisson's ratio of isotropic cement paste were subsequently calculated via [32, 33]

$$s\overline{E} = \frac{9s\overline{K}s\overline{G}}{3s\overline{K} + s\overline{G}}$$
 and  $s\overline{v} = \frac{3s\overline{K} - 2s\overline{G}}{2(3s\overline{K} + s\overline{G})}$ , (4)

where  $\overline{E}$ ,  $\overline{K}$ ,  $\overline{G}$ ,  $\overline{\nu}$  represent the Laplace transforms of apparent cement paste VE/VP Young's modulus, VE/VP bulk modulus, VE/VP shear modulus and VE/VP Poisson's ratio. The variable *s* is the Laplace transformed (time) variable.

A major challenge in predicting the VE/VP behavior of cement paste is that microstructure evolution associated with hydration (i.e., dissolution of cement phases and precipitation of hydrates) occurs over the same time scale as VE/VP relaxation. This change of internal structure leads to stress and strain redistribution inside the whole composite. A key assumption in the model discussed herein is that when there is phase change in one voxel between two successive time steps (e.g. from C<sub>3</sub>S to C-S-H), stress carried by the original phase would be redistributed to surrounding phases upon dissolution (thus increasing the stress carried by these phases), resulting in an apparent VE/VP deformation. This assumption implies that stress redistribution takes place much faster than chemical phase changes.

Meanwhile, the newly formed phases must form in a stress-free state that conforms to the preexisting deformed configuration, and no historical responses in this voxel before formation occurs should be included in the finite element calculation. As a result, apparent strain<sup>2</sup> (i.e., strain that exists independent of the state of stress) is produced inside the microstructure and information regarding apparent strain must be stored in the finite element formulation for calculation purposes. Fig. 1 elaborates conceptually the redistribution of stress and strain of an evolving microstructure under a general stress-controlled boundary condition, which yields an apparent VE/VP response. The same apparent VE/VP response appears under a strain-controlled period boundary condition, which is applied in the model. The term "apparent VE/VP" moduli is reserved for modeling the constitutive behavior at the macroscale induced by smaller length scale mechanisms that are not due to inherent VE behavior of phases within the material.

<sup>&</sup>lt;sup>2</sup> Apparent strain is defined here, from a continuum mechanics perspective, as strain that exists independent of the state of stress. Unlike free strains (e.g., strain induced by changes in temperature or moisture state of the material), the apparent strain here does not involve a change in the atomic or molecular spacing from the reference configuration. However, from a book-keeping perspective, apparent strain is treated in the same fashion as free strains.

To illustrate the process of the VE/VP model more specifically, Fig. 2 shows the simplified flow chart for the computational scheme. At the first time step in the model, a strain-controlled periodic boundary condition is applied on the microstructure of a particular age, and the finite element calculation is carried out based on historical responses of each voxel and the loading histories. For each voxel, the linearly viscoelastic constitutive relationship may be expressed as [34]

$$\sigma_{ij}(t) = \int_{0}^{t} \varepsilon_{kl}(t-s)\dot{C}_{ijkl}(s)ds = \int_{0}^{t} C_{ijkl}(t-s)\dot{\varepsilon}_{kl}(s)ds, \qquad (5)$$

where  $C_{ijkl}(t)$  are the components of the viscoelastic relaxation moduli tensor at time t. With the involvement of discretized time steps in the finite element calculation, eq. (5) may be approximated as

$$\sigma_{ij}(t_n) = \varepsilon_{kl}(t_n)C_{ijkl}(t_0) + \sum_{k=0}^{k=n-1} \varepsilon_{kl}(t_k)[C_{ijkl}(t_n - t_k) - C_{ijkl}(t_n - t_{k+1})],$$
(6)

where  $t_0$  denotes the initial time when the periodic boundary condition is applied and  $t_i$  is the time at *i*th time step. For those phases considered to be purely conservative (phases with only elastic properties), the summation in eq. (6) becomes zero. With the calculated stress and strain histories in each voxel, the total energy stored in the whole microstructure is calculated and minimized at each time step to determine the resultant stress and strain fields inside the microstructure, which are then spatially averaged to calculate the VE/VP moduli at the macroscopic scale. At each subsequent time step, the new microstructure for the age corresponding to that time step is input into the model and comparison between the previous microstructure and the current microstructure is carried out on every voxel to check for phase change. Voxels with phase change are recorded and the previous mechanical responses of such voxels are disregarded in future calculations. Furthermore, any stresses within the dissolved phase are redistributed to the surrounding voxels. The VE moduli of phase-changed voxels are relaxed according to the loading histories subsequent to the time they are formed during all the following time steps. That is, if one voxel experiences phase change at the  $i^{th}$  time step  $(t = t_0)$ , in all subsequent time steps the moduli of this specified voxel are no longer based on the mechanical properties of the previous phase, but on the current changed phase. If the voxel is switched to an elastic phase, the moduli of this voxel are kept constant in all the following time steps with the current phase elastic moduli; if the voxel is switched to a VE phase (such as C-S-H), the moduli of this voxel would be assigned a VE moduli with the relaxation starting at time  $t = t_0$ , the time at which phase change occurs, for all the following time steps. Calculations are carried out based on the renewed response histories and moduli. The second step in the routine is repeated until all time steps are complete.

**Fig. 2** *Simplified flow chart for the computational finite element procedure predicting the apparent VE/VP behavior of cement paste.* 

The computational scheme and associated material model allows investigation of relaxation caused by both intrinsic C-S-H viscoelasticity and microstructure evolution concurrently. It

also can separately model the VE/VP relaxation of cement paste due strictly to intrinsic C-S-H relaxation or the apparent VE/VP relaxation of cement paste due strictly to dissolution of certain phases. One can evaluate the contribution of intrinsic relaxation to the overall VE/VP behavior by defining a unique VE or VP constitutive property for any given phase while utilizing unchanging microstructure for all time steps or one can strictly examine the effect of microstructure evolution by utilizing time-evolving microstructures of composites with purely elastic phases. This separation allows us to judge the relative magnitude of these two sources of VE/VP behavior, as compared to experiment, which always mixes the two sources.

## 2.3. Model Validation

The advantage of the newly generated model and finite element implementation is that it is able to simulate apparent VE/VP effects that occur due to microstructure evolution while simultaneously considering intrinsic VE/VP properties associated with phases that exhibit VE/VP behavior. As far as the authors are aware, there are no commercially available FEM software packages capable of validating this novel aspect of the new software. However, a simple simulation was performed to evaluate the physical rationality of the computed results. The simulation considered a THAMES generated microstructure for a 0.40 *w/c* cement paste (simulated under an isothermal condition of 25° C) that utilized chemical and physical data for a certain well-characterized portland cement. Microstructure snapshots were taken over the course of several days of age. Each phase in the microstructure was assigned elastic properties taken from [1], except C-S-H was assigned a VE Young's modulus prescribed as  $E(t) = 11.2 + 11.2 \exp(-0.2t)$  GPa, which allows 50% of the instantaneous elastic Young's modulus to be relaxed as  $t \rightarrow \infty$ . The Poisson's ratio of the C-S-H was prescribed to be time-independent as v = 0.25. As shown in Fig. 3(a), during the first 13 days, a constant periodic

bulk strain ( $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ ) of 0.01 was applied to the composite material, and this applied strain was suddenly removed at the 13<sup>th</sup> day, forcing the material to return back to its original geometry of zero bulk strain.

**Fig. 3** Virtual experiment of 0.40 w/c cement paste with an evolving microstructure under a virtual strain controlled boundary condition. (a) Virtual applied bulk strain history with a sudden removal at  $13^{th}$  day. (b) Mechanical response (apparent volumetric stress) of viscoelastic composite material under boundary history (a). The VE Young's modulus of C-S-H was assumed to be  $E(t) = 11.2 + 11.2 \exp(-0.2t)$ GPa, where t is in days and the Poisson's ratio of C-S-H was assumed to be a constant value of 0.25. The elastic properties of all other phases were taken from [1]. As illustrated by diagrams using simplified parallel phase geometry, the sudden drop of the apparent volumetric stress into a negative magnitude was associated with the tensile pressure required to force those phases formed after the initial application of bulk strain back to a zero strain condition.

Fig. 3(b) shows the apparent macroscopic volumetric stress (the average value of  $\sigma_{11}$ ,  $\sigma_{22}$  and  $\sigma_{33}$ ) of the composite predicted by the finite element model. During the first 13 d, the composite showed smooth relaxation under constant controlled strain due to the two stress-relaxation mechanisms (i.e., phase dissolution of cement grains and intrinsic VE properties of the C-S-H), and at the 13<sup>th</sup> day, with the sudden removal of the periodic bulk strain, the volumetric stress of the material also exhibited a sudden drop. However, instead of returning back to zero as the external controlled strain did, the volumetric stress assumed a negative value. The existence of the residual stress within the composite is not unexpected. As illustrated conceptually by the diagrams in Fig. 3(b), when a controlled strain is applied, the

existing phases deform under the external boundary condition. During the hydration process, some phases inside the composite material dissolve and form new phases in the deformed configuration in a stress-free state. When the bulk strain of the microstructure was suddenly forced back to zero in the simulation, opposing stresses were necessarily generated within the latter-formed phases, leading to a negative volumetric stress. A very simple model, a spring of length L, serves to further illustrate this point. Suppose the spring is extended in tension by an amount x and held there. Another spring is added in parallel, of unextended length L' = L + x. This second spring is longer, but carries no force. When the first spring is released, it will not relax all the way back to zero extension but will retain some amount of tension since the second spring will be simultaneously pulled into compression.

### 2.4. Virtual Experiments

To further exploit the utility of the newly generated model, a sequence of virtual experiments were performed to probe the contribution of each VE/VP mechanism (intrinsic C-S-H viscoelasticity or microstructure evolution) to overall early-age VE/VP behavior of cement paste. By applying purely controlled periodic volumetric strain and purely controlled periodic shear strain on the boundary of a series of microstructures with  $100^3$  voxels (with the dimension of each voxel as  $1 \,\mu m^3$ ) at different ages, the evolution of apparent cement paste VE/VP bulk modulus and VE/VP shear modulus were simulated by the model. The apparent VE/VP Young's modulus and the apparent VE/VP Poisson's ratio were then calculated using eq. (4). All microstructures utilized in the virtual experiments were generated by THAMES on simulated sealed cement pastes of CCRL Proficiency Sample Cement 168, simulated under an isothermal, sealed condition of 25 °C (298 K) [35], and the mechanical elastic moduli of each individual phase (e.g. C<sub>3</sub>S, C-S-H) were taken from previous studies

## 3. Results and Discussion

#### 3.1. Viscoelasticity/Viscoplasticity due to Microstructure Evolution

To evaluate the apparent VE/VP behavior occurring strictly due to microstructure evolution, microstructures of cement composites with pure elastic phases (no inherent viscoelasticity) at different ages (from 1 d to 56 d) were first considered. Fig. 4 shows the predicted apparent VE/VP Young's modulus of 0.40 w/c cement paste under constant periodic strain boundary condition applied at different ages of 1 d and 7 d. The relaxation shown in Fig. 4 was due entirely to the time-dependent dissolution of cement grains. From the predicted results, one can see that the apparent VE/VP behavior caused by dissolution of cement grains is substantial. Thus, microstructure evolution associated with the hydration process should be included as a significant mechanism in cement paste VE/VP behavior. Additionally, as the rate of relaxation of cement paste slows as cement paste ages (because of the decreasing hydration rate with age), the well-known aging effect of cement paste VE/VP behavior is demonstrated by the hydration-related dissolution mechanism. Time-dependent, stressinduced dissolution of hydrates in cementitious materials might also induce apparent viscoelastic effects, but at this time it is unclear how cement composites dissolve under various external stress conditions, and thus stress-induced dissolution is not considered in this paper.

**Fig. 4** Apparent VE/VP Young's modulus of 0.40 w/c cement paste when loaded at different ages (1 d and 7 d). In this graph, apparent VE/VP behavior was considered to occur strictly due to dissolution of load bearing cement grains. The dissolution of load bearing cement grains resulted in significant apparent VE/VP behavior for the macroscopic cement pastes, and was able to account for the well-known aging effect of VE/VP behavior of cement paste.

## 3.2 Intrinsic C-S-H Viscoelasticity

To further investigate the mechanisms of cement paste VE/VP behavior, a simulation was carried out to compare the effect of intrinsic C-S-H viscoelasticity relative to dissolution effects on the overall VE/VP behavior of cement paste.

Intrinsic viscoelasticity of C-S-H has been historically regarded as the primary mechanism leading to cement paste VE/VP behavior. However, recent experimental results suggest that C-S-H may not exhibit as much creep and relaxation as previously thought [36]. A clear demonstration is required to show the contribution of C-S-H intrinsic viscoelasticity towards overall cement paste VE/VP properties. Thus, a simulation was performed where dissolution effects were ignored and periodic boundary conditions were applied onto non-aging microstructures; that is, the microstructures did not evolve with time during the simulation and the simulated cement paste relaxation was due entirely to inherent C-S-H viscoelasticity. Since, due to experimental challenges, there are no sufficient data currently available for modeling creep or relaxation of the C-S-H was assumed to be

 $E(t) = 11.2 + 11.2 \exp(-0.2t)GPa$ , where *t* is in unit of days and the Poisson's ratio of C-S-H was set to be a time-independent constant value of 0.2. All other phases in the microstructure were assigned to be elastic with properties taken from [1]. Fig. 5 shows the apparent VE

Young's modulus associated with the response of 0.45 w/c paste, where the relaxation was due strictly to the intrinsic viscoelastic relaxation of C-S-H.

**Fig. 5** VE Young's modulus for 0.45 w/c cement paste at different ages (1 d old and 28 d old) when the dissolution effect was ignored. The VE Young's modulus of C-S-H was assumed to be  $E(t) = 11.2 + 11.2 \exp(-0.2t)GPa$ , where t is in days and the Poisson's ratio of C-S-H was assumed to be a constant value of 0.2. The elastic properties of all other phases were taken from [1]. In this graph, all relaxation was due to intrinsic C-S-H viscoelastic relaxation.

In Fig. 5, the 1 d cement paste VE/VP Young's modulus was generated by utilizing the 1 d microstructure, and the 28 d VE/VP cement paste Young's modulus was generated by utilizing the 28 d microstructure. After periodic strain boundary conditions were applied, microstructures were no longer allowed to evolve with time. As a result, in these simulations only the VE properties of C-S-H induced relaxation in the bulk cement paste.

According to the simulation results, a 28 d cement paste would exhibit more relaxation than a 1 d cement paste. The reason behind the predicted higher relaxation for older materials is that as volume fraction of C-S-H increases with age, so does the fraction of the stress transmitted by C-S-H. If C-S-H is the only phase in cement paste able to relax stress, more C-S-H would thus result in more overall stress relaxation. However, these predictions are in contrast to existing experimental evidence [37, 38], which shows that relaxation or creep rates decrease with age (i.e., the previously mentioned aging effect). Therefore, according to these

simulations, C-S-H relaxation cannot be the primary mechanism of early-age cement paste VE/VP behavior unless the VE properties of the C-S-H itself dramatically change with age. If C-S-H phases experience significant aging, the functions for C-S-H VE moduli must vary relative to the age when specific particles of C-S-H are formed. This effect was not present in the current model.

### 3.3. Predicted Effects of Different w/c

To investigate the influence of different values of w/c on the apparent VE/VP Young's modulus at different loading ages, microstructures of cement paste with purely elastic phases (with elastic properties taken from [1]) and w/c from 0.35 to 0.50 were utilized. In this set of simulations, the VE/VP relaxation of cement paste occurred strictly due to dissolution of load bearing cement grains. Fig. 6 shows the predicted results of apparent VE/VP Young's modulus for different values of w/c as well as the normalized apparent VE/VP Young's modulus, which are normalized by the instantaneous elastic Young's modulus at loading ages of 1 d and 7 d. As shown in Fig. 6(a) and Fig. 6(b), older cement pastes establish lower relaxation rates for all different w/c considered because of the decreasing hydration rate (and thus dissolution rate) with age, which is consistent with the discussion in previous sections and experimental results. According to Fig. 6(c) and Fig. 6(d), at an early age of 1 d, the normalized results clearly show that lower w/c results in a greater percent relaxation than higher w/c. This simulation result agrees with experimental data from Vichit-Vadakan and Scherer [37], which shows that lower w/c cement pastes experience larger relaxation than higher w/c pastes at early ages. According to the model discussed here, this experimentally observed ranking may occur because dissolution of load bearing cement grains is the dominant factor affecting the relaxation rate at early ages due to the high rate of hydration.

As low w/c generates higher hydration rate at early age, a larger relaxation rate with low w/c paste is observed. At later loading ages, on the other hand, higher w/c results in larger relaxation [2]. This larger relaxation for higher w/c at later ages is likely due in part to the lower fraction of solid phases in high w/c cement pastes, which results in a smaller volume of available stress transferring phases. That is, when load bearing cement grains within a high w/c paste dissolve during a single time step, there would be a lower volume of previously formed solid phases (because of the high w/c) sharing the redistributed stress, leading to a higher relaxation rate.

**Fig. 6** Apparent viscoelastic Young' modulus for different w/c at loading age of (a) 1 d and (b) 7 d and normalized apparent VE/VP relaxation at loading age of (c) 1 d and (d) 7 d, where apparent VE/VP Young's modulus E(t) was normalized by instantaneous elastic Young's modulus. VE/VP behavior was considered to occur strictly due to microstructure evolution.

## 3.4 Evolution of Stresses

Besides the prediction of the effect of age and w/c on the apparent VE/VP properties of cement paste, predictions of the evolution of stresses (volumetric stress and deviatoric stress) carried by different phases (hydrated phases and unhydrated phases) inside cement paste composites also become achievable through the computational scheme.

Volumetric stress is the stress tending to change the volume of the body, with magnitude given by

$$p = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} = \frac{I_1}{3},$$
(7)

where *p* is the volumetric stress,  $I_i$  are the three invariants of the stress tensor and  $\sigma_{11}, \sigma_{22}, \sigma_{33}$  are normal stresses.

Deviatoric stress is the stress tending to distort the stressed body. Components of the stress deviator tensor are given by

$$[s_{ij}] = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} = \begin{pmatrix} \sigma_{11} - p & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} - p & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} - p \end{pmatrix},$$
(8)

where  $s_{ij}$  is deviatoric stress, and  $\sigma_{ij}$  are the components of the overall stress tensor. A scalar measure of deviatoric stress magnitude is

$$s = \sqrt{\frac{1}{2} s_{ij} s_{ji}} = \sqrt{\frac{1}{3} I_1^2 - I_2} , \qquad (9)$$

where *s* is the scalar deviatoric stress and i, j = 1, 2, or 3.

Since both volumetric stress and deviatoric stress are closely related to the three invariants of the stress tensor, their evolution with time can be representative of the corresponding evolutions of the general stress distribution inside the microstructure. Fig. 7 shows the predicted evolution of p and s carried by hydrated phases and unhydrated phases at different ages. In this figure, p for each phase is normalized by total volumetric stress

carried by the whole microstructure and *s* for each phase is normalized by total deviatoric stress carried by the whole microstructure. The normalization is expressed according to

$$\sigma(t)_{N} = \frac{\sum \sigma_{hydrated/unhydrated}(t)}{<\sigma(t)>}$$
(10)

where  $\sigma(t)_N$  is either normalized volumetric or deviatoric stress at time *t*,

 $\sum \sigma_{hydrated/unhydrated}(t)$  is the summed volumetric or deviatoric stress over hydrated or unhydrated voxels at time t, and  $\langle \sigma(t) \rangle$  is the integrated volumetric or deviatoric stress over the whole volume of the microstructure at time t. Microstructures constructed considering 0.40 w/c with pure elastic phases at different ages were utilized in the model, and the elastic properties of all phases were taken from [1].

**Fig. 7** Normalized volumetric stress and deviatoric stress carried by hydrated phases and unhydrated phases inside cement paste microstructure under loading age of 1 d. The summed volumetric and deviatoric stresses carried by hydrated phases and unhydrated phases at time t are normalized by total volumetric stress or total deviatoric stress carried by the whole microstructure at time t, respectively.

As C-S-H creep and relaxation has historically been considered the dominant mechanism leading to cement paste creep and relaxation, some constitutive models, such as the solidification theory [39], have been developed based on this understanding. Although the solidification theory appears to have been developed with a uniaxial stress state in mind [40], under any specific boundary conditions, evolutions of volumetric stress and deviatoric stress with time should all be capable of representing the general stress evolutions inside the microstructure, as discussed in previous paragraphs of this section. Due to equilibrium requirements, the normalized, spatially averaged stress carried by the solidified products (equivalent to hydration products) in the solidification theory may be calculated through

$$\sigma(t) = \frac{\sigma_{total}(t)}{v(t)}$$
(11)

where v(t) is the aging function describing the volume fraction of solidified phases, and  $\sigma_{total}(t)$  is the normalized total stress, either volumetric stress or deviatoric stress, predicted by the present model. Note that the solidification theory does not allow for any stress being carried by the unhydrated cement, even after the cement paste has set. From a simple composite theory view, it is clear that if solid phases are connected to the main solid backbone, they will carry load. Computations have shown that at lower values of w/c, the effective elastic moduli are significantly affected by the unhydrated cement [1].

For comparison purposes, the curves of normalized stresses carried by solidified phases calculated via the new model presented in this paper are obtained by summing all normalized stresses carried by the phases that solidify after load is applied. The evolution of stresses carried by the hydration products after the application of load (at age of 1 d) as predicted by the solidification theory and the new model are shown together in Fig. 8. The predictions considered a 0.40 w/c cement paste hydrating under isothermal conditions (25° C).

**Fig. 8** Comparison between the new model developed herein and the solidification theory regarding normalized (a) volumetric and (b) deviatoric stress carried by solidified phases (hydration products). The stresses are normalized by instantaneous total stress carried by the microstructure.

The solidification theory predicts that the average stress carried by solidified or hydrated phases decreases with time, which results from the presumption that only solidified phases may transmit stress. The solidification theory implies that hydration products are non-aging viscoelastic materials and aging arises in the bulk scale due to the increase in load bearing materials as a result of solidification and deposition of hydration products. As hydration progresses, each newly formed layer of the hydration products solidifies in a stress-free state and these layers are only subject to loads after they form. As a result of the predicted decrease in stress carried by solidified phases (including C-S-H) as hydration progresses, the solidification theory can account for the early-age aging effect through reduced C-S-H creep as stress in that phase decreases. However, according to the model developed herein and as shown in Fig. 7, the total stress carried by solidified phases increases with age. This increase occurs because the new model accounts for the fact that stress may be transmitted by both hydrated and unhydrated phases (hydrostatic stresses may be transmitted by cement grains at any age, while deviatoric stresses may only be transmitted once percolation of the solid skeleton has occurred). Since unhydrated phases are allowed to carry stress, their dissolution results in an increase in stress on hydration products. Thus, the solidification theory is only able to capture early-age aging effects while considering C-S-H viscoelasticity as a primary mechanism for early-age cement paste creep and relaxation because the ability of cement grains to transmit stress is neglected.

#### 4. Conclusions

A computational scheme that couples a microstructure evolution model and a time-stepping finite element method capable of tracking phase formation is developed in this paper to predict the apparent VE/VP properties of cement paste as a function of time-evolving

microstructures. From the model simulations, the apparent VE/VP behavior of hydrating cement paste due to dissolution of cement grains is a significant factor in the overall early-age creep and relaxation of the paste. The main reasons behind this are the stress transmission from dissolved load bearing phases to surrounding hydrated phases or cement grains, and the generation of apparent strain in the new components that form in deformed configurations (i.e., the newly formed phases have a deformation gradient but no stress). Simulation results also indicate that intrinsic C-S-H viscoelasticity is not likely the primary mechanism leading to the early-age creep and relaxation behavior of cementitious materials; this is because significant C-S-H relaxation results in simulated macroscopic behavior that is in conflict with experimental evidence of early-age aging effects.

The comparison between the evolution of stresses within hydration products predicted by the new computational scheme and that predicted by the solidification theory indicates that the specific assumption made about the extent to which unhydrated phases can transmit stress is key to interpreting VE/VP mechanisms of cement paste. If one stipulates that unhydrated phases do not carry stress (as with the solidification theory), then increased formation of C-S-H can lead to aging of VE/VP properties of cement paste (e.g., reductions in creep or relaxation rates at later ages). However, as demonstrated by the new computational scheme and model presented herein, if one presumes that unhydrated phases may transmit stress once the solid phases form a percolated network, then their dissolution results in an increase in stress on hydration products as hydration progresses. This increase in stress in the less stiff hydration products results in a greater relaxation rate, counteracting any reduction in rate due to the increased formation of C-S-H; thus, the formation of C-S-H does not act as a source of aging of VE/VP properties of cement paste. Conversely, the slowing of the cement

dissolution process (associated with the hydration reaction) with time may lead to lower creep and relaxation rates of cement paste at later ages, contributing strongly to the early age aging of cement paste.

The model discussed in this paper is yet unable to fully explain certain observed VE/VP behavior of cement paste, including overall observed magnitude and differences between responses associated with tensile and compressive stresses. Thus, additional mechanisms must be considered in addition to hydration induced cement grain dissolution.

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Unhydrated material

Newly formed material

Water













**ոց = 3** 

(b)

(a)

Figure3





















# 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.

Keywords: C-S-H [B]; Finite Element Analysis [C]; Microstructure [B]; Viscoelastic; Dissolution; THAMES

## 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.

### 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 hrs 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.<sup>1</sup> 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  $\Omega$  of the problem, the virtual work expression for stored mechanical energy is derived under a virtual stress boundary condition induced by the traction condition

<sup>&</sup>lt;sup>1</sup> 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.

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

for all points lying on a part of the boundary denoted as  $S_2$ , where  $\sigma_{ij}$  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

$$\int_{\Omega} \delta u_i b_i d\Omega + \int_{S_2} \delta u_i t_i d\Omega - \int_{\Omega} \delta u_i \rho \ddot{u_i} d\Omega - \int_{\Omega} \delta \varepsilon_{ij} \sigma_{ij} d\Omega = 0, \qquad (2)$$

where  $\rho$  is mass density,  $b_i$  are body force components,  $u_i$  are displacement components,  $\varepsilon_{ij}$  are infinitesimal strain components,  $\delta$  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

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

where  $\psi$  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.

**Fig. 1** Conceptual diagram of model simulating apparent VE/VP behavior of hydrating cement paste due to microstructure evolution, where  $\sigma$  is an applied external macroscale stress and t is time elapsed. (a) Before application of load, there exists a certain amount of unhydrated phases. (b) Load is applied and existing components deform due to elastic mechanical properties. (c) Hydration occurs and some unhydrated load bearing cement grains dissolve, increasing the stress in surrounding phases. Stress and strain redistributes to maintain the boundary condition and the overall deformation field of the composite microstructure changes. Even if nearby phases are purely elastic, the overall change of deformation depends on when dissolution occurs, resulting in apparent VE/VP behavior. (d) New components form in the deformed configuration with apparent strain and zero stress.

Prescribed, periodic volumetric strain and prescribed, periodic shear strain were applied on the boundaries of a series of microstructures at different ages to determine the evolutions of cement paste VE/VP bulk modulus and VE/VP shear modulus. The expressions were subjected to Laplace transformations to determine the VE/VP Young's modulus and Poisson's ratio from the VE/VP bulk and shear moduli. The resultant VE/VP Young's modulus and VE/VP Poisson's ratio of isotropic cement paste were subsequently calculated via [32, 33]

$$s\overline{E} = \frac{9s\overline{K}s\overline{G}}{3s\overline{K} + s\overline{G}}$$
 and  $s\overline{v} = \frac{3s\overline{K} - 2s\overline{G}}{2(3s\overline{K} + s\overline{G})}$ , (4)

where  $\overline{E}$ ,  $\overline{K}$ ,  $\overline{G}$ ,  $\overline{\nu}$  represent the Laplace transforms of apparent cement paste VE/VP Young's modulus, VE/VP bulk modulus, VE/VP shear modulus and VE/VP Poisson's ratio. The variable *s* is the Laplace transformed (time) variable.

A major challenge in predicting the VE/VP behavior of cement paste is that microstructure evolution associated with hydration (i.e., dissolution of cement phases and precipitation of hydrates) occurs over the same time scale as VE/VP relaxation. This change of internal structure leads to stress and strain redistribution inside the whole composite. A key assumption in the model discussed herein is that when there is phase change in one voxel between two successive time steps (e.g. from C<sub>3</sub>S to C-S-H), stress carried by the original phase would be redistributed to surrounding phases upon dissolution (thus increasing the stress carried by these phases), resulting in an apparent VE/VP deformation. This assumption implies that stress redistribution takes place much faster than chemical phase changes.

Meanwhile, the newly formed phases must form in a stress-free state that conforms to the preexisting deformed configuration, and no historical responses in this voxel before formation occurs should be included in the finite element calculation. As a result, apparent strain<sup>2</sup> (i.e., strain that exists independent of the state of stress) is produced inside the microstructure and information regarding apparent strain must be stored in the finite element formulation for calculation purposes. Fig. 1 elaborates conceptually the redistribution of stress and strain of an evolving microstructure under a general stress-controlled boundary condition, which yields an apparent VE/VP response. The same apparent VE/VP response appears under a strain-controlled period boundary condition, which is applied in the model. The term "apparent VE/VP" moduli is reserved for modeling the constitutive behavior at the macroscale induced by smaller length scale mechanisms that are not due to inherent VE behavior of phases within the material.

<sup>&</sup>lt;sup>2</sup> Apparent strain is defined here, from a continuum mechanics perspective, as strain that exists independent of the state of stress. Unlike free strains (e.g., strain induced by changes in temperature or moisture state of the material), the apparent strain here does not involve a change in the atomic or molecular spacing from the reference configuration. However, from a book-keeping perspective, apparent strain is treated in the same fashion as free strains.

To illustrate the process of the VE/VP model more specifically, Fig. 2 shows the simplified flow chart for the computational scheme. At the first time step in the model, a strain-controlled periodic boundary condition is applied on the microstructure of a particular age, and the finite element calculation is carried out based on historical responses of each voxel and the loading histories. For each voxel, the linearly viscoelastic constitutive relationship may be expressed as [34]

$$\sigma_{ij}(t) = \int_{0}^{t} \varepsilon_{kl}(t-s)\dot{C}_{ijkl}(s)ds = \int_{0}^{t} C_{ijkl}(t-s)\dot{\varepsilon}_{kl}(s)ds, \qquad (5)$$

where  $C_{ijkl}(t)$  are the components of the viscoelastic relaxation moduli tensor at time t. With the involvement of discretized time steps in the finite element calculation, eq. (5) may be approximated as

$$\sigma_{ij}(t_n) = \varepsilon_{kl}(t_n)C_{ijkl}(t_0) + \sum_{k=0}^{k=n-1} \varepsilon_{kl}(t_k)[C_{ijkl}(t_n - t_k) - C_{ijkl}(t_n - t_{k+1})],$$
(6)

where  $t_0$  denotes the initial time when the periodic boundary condition is applied and  $t_i$  is the time at *i*th time step. For those phases considered to be purely conservative (phases with only elastic properties), the summation in eq. (6) becomes zero. With the calculated stress and strain histories in each voxel, the total energy stored in the whole microstructure is calculated and minimized at each time step to determine the resultant stress and strain fields inside the microstructure, which are then spatially averaged to calculate the VE/VP moduli at the macroscopic scale. At each subsequent time step, the new microstructure for the age corresponding to that time step is input into the model and comparison between the previous microstructure and the current microstructure is carried out on every voxel to check for phase change. Voxels with phase change are recorded and the previous mechanical responses of such voxels are disregarded in future calculations. Furthermore, any stresses within the dissolved phase are redistributed to the surrounding voxels. The VE moduli of phase-changed voxels are relaxed according to the loading histories subsequent to the time they are formed during all the following time steps. That is, if one voxel experiences phase change at the  $i^{th}$  time step  $(t = t_0)$ , in all subsequent time steps the moduli of this specified voxel are no longer based on the mechanical properties of the previous phase, but on the current changed phase. If the voxel is switched to an elastic phase, the moduli of this voxel are kept constant in all the following time steps with the current phase elastic moduli; if the voxel is switched to a VE phase (such as C-S-H), the moduli of this voxel would be assigned a VE moduli with the relaxation starting at time  $t = t_0$ , the time at which phase change occurs, for all the following time steps. Calculations are carried out based on the renewed response histories and moduli. The second step in the routine is repeated until all time steps are complete.

**Fig. 2** *Simplified flow chart for the computational finite element procedure predicting the apparent VE/VP behavior of cement paste.* 

The computational scheme and associated material model allows investigation of relaxation caused by both intrinsic C-S-H viscoelasticity and microstructure evolution concurrently. It

also can separately model the VE/VP relaxation of cement paste due strictly to intrinsic C-S-H relaxation or the apparent VE/VP relaxation of cement paste due strictly to dissolution of certain phases. One can evaluate the contribution of intrinsic relaxation to the overall VE/VP behavior by defining a unique VE or VP constitutive property for any given phase while utilizing unchanging microstructure for all time steps or one can strictly examine the effect of microstructure evolution by utilizing time-evolving microstructures of composites with purely elastic phases. This separation allows us to judge the relative magnitude of these two sources of VE/VP behavior, as compared to experiment, which always mixes the two sources.

## 2.3. Model Validation

The advantage of the newly generated model and finite element implementation is that it is able to simulate apparent VE/VP effects that occur due to microstructure evolution while simultaneously considering intrinsic VE/VP properties associated with phases that exhibit VE/VP behavior. As far as the authors are aware, there are no commercially available FEM software packages capable of validating this novel aspect of the new software. However, a simple simulation was performed to evaluate the physical rationality of the computed results. The simulation considered a THAMES generated microstructure for a 0.40 *w/c* cement paste (simulated under an isothermal condition of 25° C) that utilized chemical and physical data for a certain well-characterized portland cement. Microstructure snapshots were taken over the course of several days of age. Each phase in the microstructure was assigned elastic properties taken from [1], except C-S-H was assigned a VE Young's modulus prescribed as  $E(t) = 11.2 + 11.2 \exp(-0.2t)$  GPa , which allows 50% of the instantaneous elastic Young's modulus to be relaxed as  $t \rightarrow \infty$ . The Poisson's ratio of the C-S-H was prescribed to be time-independent as v = 0.25. As shown in Fig. 3(a), during the first 13 days, a constant periodic

bulk strain ( $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ ) of 0.01 was applied to the composite material, and this applied strain was suddenly removed at the 13<sup>th</sup> day, forcing the material to return back to its original geometry of zero bulk strain.

**Fig. 3** Virtual experiment of 0.40 w/c cement paste with an evolving microstructure under a virtual strain controlled boundary condition. (a) Virtual applied bulk strain history with a sudden removal at  $13^{th}$  day. (b) Mechanical response (apparent volumetric stress) of viscoelastic composite material under boundary history (a). The VE Young's modulus of C-S-H was assumed to be  $E(t) = 11.2 + 11.2 \exp(-0.2t)$ GPa, where t is in days and the Poisson's ratio of C-S-H was assumed to be a constant value of 0.25. The elastic properties of all other phases were taken from [1]. As illustrated by diagrams using simplified parallel phase geometry, the sudden drop of the apparent volumetric stress into a negative magnitude was associated with the tensile pressure required to force those phases formed after the initial application of bulk strain back to a zero strain condition.

Fig. 3(b) shows the apparent macroscopic volumetric stress (the average value of  $\sigma_{11}$ ,  $\sigma_{22}$  and  $\sigma_{33}$ ) of the composite predicted by the finite element model. During the first 13 d, the composite showed smooth relaxation under constant controlled strain due to the two stress-relaxation mechanisms (i.e., phase dissolution of cement grains and intrinsic VE properties of the C-S-H), and at the 13<sup>th</sup> day, with the sudden removal of the periodic bulk strain, the volumetric stress of the material also exhibited a sudden drop. However, instead of returning back to zero as the external controlled strain did, the volumetric stress assumed a negative value. The existence of the residual stress within the composite is not unexpected. As illustrated conceptually by the diagrams in Fig. 3(b), when a controlled strain is applied, the

existing phases deform under the external boundary condition. During the hydration process, some phases inside the composite material dissolve and form new phases in the deformed configuration in a stress-free state. When the bulk strain of the microstructure was suddenly forced back to zero in the simulation, opposing stresses were necessarily generated within the latter-formed phases, leading to a negative volumetric stress. A very simple model, a spring of length L, serves to further illustrate this point. Suppose the spring is extended in tension by an amount x and held there. Another spring is added in parallel, of unextended length L' = L + x. This second spring is longer, but carries no force. When the first spring is released, it will not relax all the way back to zero extension but will retain some amount of tension since the second spring will be simultaneously pulled into compression.

### 2.4. Virtual Experiments

To further exploit the utility of the newly generated model, a sequence of virtual experiments were performed to probe the contribution of each VE/VP mechanism (intrinsic C-S-H viscoelasticity or microstructure evolution) to overall early-age VE/VP behavior of cement paste. By applying purely controlled periodic volumetric strain and purely controlled periodic shear strain on the boundary of a series of microstructures with 100<sup>3</sup> voxels (with the dimension of each voxel as 1  $\mu$ m<sup>3</sup>) at different ages, the evolution of apparent cement paste VE/VP bulk modulus and VE/VP shear modulus were simulated by the model. The apparent VE/VP Young's modulus and the apparent VE/VP Poisson's ratio were then calculated using eq. (4). All microstructures utilized in the virtual experiments were generated by THAMES on simulated sealed cement pastes of CCRL Proficiency Sample Cement 168, simulated under an isothermal, sealed condition of 25 °C (298 K) [35], and the mechanical elastic moduli of each individual phase (e.g. C<sub>3</sub>S, C-S-H) were taken from previous studies

elaborated in [1]. The cement composite microstructures considered different values of w/c varying from 0.35 to 0.50, and ages from 1 d to 56 d.

## 3. Results and Discussion

#### 3.1. Viscoelasticity/Viscoplasticity due to Microstructure Evolution

To evaluate the apparent VE/VP behavior occurring strictly due to microstructure evolution, microstructures of cement composites with pure elastic phases (no inherent viscoelasticity) at different ages (from 1 d to 56 d) were first considered. Fig. 4 shows the predicted apparent VE/VP Young's modulus of 0.40 w/c cement paste under constant periodic strain boundary condition applied at different ages of 1 d and 7 d. The relaxation shown in Fig. 4 was due entirely to the time-dependent dissolution of cement grains. From the predicted results, one can see that the apparent VE/VP behavior caused by dissolution of cement grains is substantial. Thus, microstructure evolution associated with the hydration process should be included as a significant mechanism in cement paste VE/VP behavior. Additionally, as the rate of relaxation of cement paste slows as cement paste ages (because of the decreasing hydration rate with age), the well-known aging effect of cement paste VE/VP behavior is demonstrated by the hydration-related dissolution mechanism. Time-dependent, stressinduced dissolution of hydrates in cementitious materials might also induce apparent viscoelastic effects, but at this time it is unclear how cement composites dissolve under various external stress conditions, and thus stress-induced dissolution is not considered in this paper.

**Fig. 4** Apparent VE/VP Young's modulus of 0.40 w/c cement paste when loaded at different ages (1 d and 7 d). In this graph, apparent VE/VP behavior was considered to occur strictly due to dissolution of load bearing cement grains. The dissolution of load bearing cement grains resulted in significant apparent VE/VP behavior for the macroscopic cement pastes, and was able to account for the well-known aging effect of VE/VP behavior of cement paste.

## 3.2 Intrinsic C-S-H Viscoelasticity

To further investigate the mechanisms of cement paste VE/VP behavior, a simulation was carried out to compare the effect of intrinsic C-S-H viscoelasticity relative to dissolution effects on the overall VE/VP behavior of cement paste.

Intrinsic viscoelasticity of C-S-H has been historically regarded as the primary mechanism leading to cement paste VE/VP behavior. However, recent experimental results suggest that C-S-H may not exhibit as much creep and relaxation as previously thought [36]. A clear demonstration is required to show the contribution of C-S-H intrinsic viscoelasticity towards overall cement paste VE/VP properties. Thus, a simulation was performed where dissolution effects were ignored and periodic boundary conditions were applied onto non-aging microstructures; that is, the microstructures did not evolve with time during the simulation and the simulated cement paste relaxation was due entirely to inherent C-S-H viscoelasticity. Since, due to experimental challenges, there are no sufficient data currently available for modeling creep or relaxation of the C-S-H was assumed to be

 $E(t) = 11.2 + 11.2 \exp(-0.2t)GPa$ , where *t* is in unit of days and the Poisson's ratio of C-S-H was set to be a time-independent constant value of 0.2. All other phases in the microstructure were assigned to be elastic with properties taken from [1]. Fig. 5 shows the apparent VE

Young's modulus associated with the response of 0.45 w/c paste, where the relaxation was due strictly to the intrinsic viscoelastic relaxation of C-S-H.

**Fig. 5** VE Young's modulus for 0.45 w/c cement paste at different ages (1 d old and 28 d old) when the dissolution effect was ignored. The VE Young's modulus of C-S-H was assumed to be  $E(t) = 11.2 + 11.2 \exp(-0.2t)GPa$ , where t is in days and the Poisson's ratio of C-S-H was assumed to be a constant value of 0.2. The elastic properties of all other phases were taken from [1]. In this graph, all relaxation was due to intrinsic C-S-H viscoelastic relaxation.

In Fig. 5, the 1 d cement paste VE/VP Young's modulus was generated by utilizing the 1 d microstructure, and the 28 d VE/VP cement paste Young's modulus was generated by utilizing the 28 d microstructure. After periodic strain boundary conditions were applied, microstructures were no longer allowed to evolve with time. As a result, in these simulations only the VE properties of C-S-H induced relaxation in the bulk cement paste.

According to the simulation results, a 28 d cement paste would exhibit more relaxation than a 1 d cement paste. The reason behind the predicted higher relaxation for older materials is that as volume fraction of C-S-H increases with age, so does the fraction of the stress transmitted by C-S-H. If C-S-H is the only phase in cement paste able to relax stress, more C-S-H would thus result in more overall stress relaxation. However, these predictions are in contrast to existing experimental evidence [37, 38], which shows that relaxation or creep rates decrease with age (i.e., the previously mentioned aging effect). Therefore, according to these

simulations, C-S-H relaxation cannot be the primary mechanism of early-age cement paste VE/VP behavior unless the VE properties of the C-S-H itself dramatically change with age. If C-S-H phases experience significant aging, the functions for C-S-H VE moduli must vary relative to the age when specific particles of C-S-H are formed. This effect was not present in the current model.

## 3.3. Predicted Effects of Different w/c

To investigate the influence of different values of w/c on the apparent VE/VP Young's modulus at different loading ages, microstructures of cement paste with purely elastic phases (with elastic properties taken from [1]) and w/c from 0.35 to 0.50 were utilized. In this set of simulations, the VE/VP relaxation of cement paste occurred strictly due to dissolution of load bearing cement grains. Fig. 6 shows the predicted results of apparent VE/VP Young's modulus for different values of w/c as well as the normalized apparent VE/VP Young's modulus, which are normalized by the instantaneous elastic Young's modulus at loading ages of 1 d and 7 d. As shown in Fig. 6(a) and Fig. 6(b), older cement pastes establish lower relaxation rates for all different w/c considered because of the decreasing hydration rate (and thus dissolution rate) with age, which is consistent with the discussion in previous sections and experimental results. According to Fig. 6(c) and Fig. 6(d), at an early age of 1 d, the normalized results clearly show that lower w/c results in a greater percent relaxation than higher w/c. This simulation result agrees with experimental data from Vichit-Vadakan and Scherer [37], which shows that lower w/c cement pastes experience larger relaxation than higher w/c pastes at early ages. According to the model discussed here, this experimentally observed ranking may occur because dissolution of load bearing cement grains is the dominant factor affecting the relaxation rate at early ages due to the high rate of hydration.

As low w/c generates higher hydration rate at early age, a larger relaxation rate with low w/c paste is observed. At later loading ages, on the other hand, higher w/c results in larger relaxation [2]. This larger relaxation for higher w/c at later ages is likely due in part to the lower fraction of solid phases in high w/c cement pastes, which results in a smaller volume of available stress transferring phases. That is, when load bearing cement grains within a high w/c paste dissolve during a single time step, there would be a lower volume of previously formed solid phases (because of the high w/c) sharing the redistributed stress, leading to a higher relaxation rate.

**Fig. 6** Apparent viscoelastic Young' modulus for different w/c at loading age of (a) 1 d and (b) 7 d and normalized apparent VE/VP relaxation at loading age of (c) 1 d and (d) 7 d, where apparent VE/VP Young's modulus E(t) was normalized by instantaneous elastic Young's modulus. VE/VP behavior was considered to occur strictly due to microstructure evolution.

## 3.4 Evolution of Stresses

Besides the prediction of the effect of age and w/c on the apparent VE/VP properties of cement paste, predictions of the evolution of stresses (volumetric stress and deviatoric stress) carried by different phases (hydrated phases and unhydrated phases) inside cement paste composites also become achievable through the computational scheme.

Volumetric stress is the stress tending to change the volume of the body, with magnitude given by

$$p = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} = \frac{I_1}{3},$$
(7)

where *p* is the volumetric stress,  $I_i$  are the three invariants of the stress tensor and  $\sigma_{11}, \sigma_{22}, \sigma_{33}$  are normal stresses.

Deviatoric stress is the stress tending to distort the stressed body. Components of the stress deviator tensor are given by

$$[s_{ij}] = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{pmatrix} = \begin{pmatrix} \sigma_{11} - p & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} - p & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} - p \end{pmatrix},$$
(8)

where  $s_{ij}$  is deviatoric stress, and  $\sigma_{ij}$  are the components of the overall stress tensor. A scalar measure of deviatoric stress magnitude is

$$s = \sqrt{\frac{1}{2} s_{ij} s_{ji}} = \sqrt{\frac{1}{3} I_1^2 - I_2} , \qquad (9)$$

where *s* is the scalar deviatoric stress and i, j = 1, 2, or 3.

Since both volumetric stress and deviatoric stress are closely related to the three invariants of the stress tensor, their evolution with time can be representative of the corresponding evolutions of the general stress distribution inside the microstructure. Fig. 7 shows the predicted evolution of p and s carried by hydrated phases and unhydrated phases at different ages. In this figure, p for each phase is normalized by total volumetric stress

carried by the whole microstructure and *s* for each phase is normalized by total deviatoric stress carried by the whole microstructure. The normalization is expressed according to

$$\sigma(t)_{N} = \frac{\sum \sigma_{hydrated/unhydrated}(t)}{<\sigma(t)>}$$
(10)

where  $\sigma(t)_N$  is either normalized volumetric or deviatoric stress at time *t*,

 $\sum \sigma_{hydrated/unhydrated}(t)$  is the summed volumetric or deviatoric stress over hydrated or unhydrated voxels at time t, and  $\langle \sigma(t) \rangle$  is the integrated volumetric or deviatoric stress over the whole volume of the microstructure at time t. Microstructures constructed considering 0.40 w/c with pure elastic phases at different ages were utilized in the model, and the elastic properties of all phases were taken from [1].

**Fig. 7** Normalized volumetric stress and deviatoric stress carried by hydrated phases and unhydrated phases inside cement paste microstructure under loading age of 1 d. The summed volumetric and deviatoric stresses carried by hydrated phases and unhydrated phases at time t are normalized by total volumetric stress or total deviatoric stress carried by the whole microstructure at time t, respectively.

As C-S-H creep and relaxation has historically been considered the dominant mechanism leading to cement paste creep and relaxation, some constitutive models, such as the solidification theory [39], have been developed based on this understanding. Although the solidification theory appears to have been developed with a uniaxial stress state in mind [40], under any specific boundary conditions, evolutions of volumetric stress and deviatoric stress with time should all be capable of representing the general stress evolutions inside the microstructure, as discussed in previous paragraphs of this section. Due to equilibrium requirements, the normalized, spatially averaged stress carried by the solidified products (equivalent to hydration products) in the solidification theory may be calculated through

$$\sigma(t) = \frac{\sigma_{total}(t)}{v(t)}$$
(11)

where v(t) is the aging function describing the volume fraction of solidified phases, and  $\sigma_{total}(t)$  is the normalized total stress, either volumetric stress or deviatoric stress, predicted by the present model. Note that the solidification theory does not allow for any stress being carried by the unhydrated cement, even after the cement paste has set. From a simple composite theory view, it is clear that if solid phases are connected to the main solid backbone, they will carry load. Computations have shown that at lower values of w/c, the effective elastic moduli are significantly affected by the unhydrated cement [1].

For comparison purposes, the curves of normalized stresses carried by solidified phases calculated via the new model presented in this paper are obtained by summing all normalized stresses carried by the phases that solidify after load is applied. The evolution of stresses carried by the hydration products after the application of load (at age of 1 d) as predicted by the solidification theory and the new model are shown together in Fig. 8. The predictions considered a 0.40 w/c cement paste hydrating under isothermal conditions (25° C).

**Fig. 8** Comparison between the new model developed herein and the solidification theory regarding normalized (a) volumetric and (b) deviatoric stress carried by solidified phases (hydration products). The stresses are normalized by instantaneous total stress carried by the microstructure.

The solidification theory predicts that the average stress carried by solidified or hydrated phases decreases with time, which results from the presumption that only solidified phases may transmit stress. The solidification theory implies that hydration products are non-aging viscoelastic materials and aging arises in the bulk scale due to the increase in load bearing materials as a result of solidification and deposition of hydration products. As hydration progresses, each newly formed layer of the hydration products solidifies in a stress-free state and these layers are only subject to loads after they form. As a result of the predicted decrease in stress carried by solidified phases (including C-S-H) as hydration progresses, the solidification theory can account for the early-age aging effect through reduced C-S-H creep as stress in that phase decreases. However, according to the model developed herein and as shown in Fig. 7, the total stress carried by solidified phases increases with age. This increase occurs because the new model accounts for the fact that stress may be transmitted by both hydrated and unhydrated phases (hydrostatic stresses may be transmitted by cement grains at any age, while deviatoric stresses may only be transmitted once percolation of the solid skeleton has occurred). Since unhydrated phases are allowed to carry stress, their dissolution results in an increase in stress on hydration products. Thus, the solidification theory is only able to capture early-age aging effects while considering C-S-H viscoelasticity as a primary mechanism for early-age cement paste creep and relaxation because the ability of cement grains to transmit stress is neglected.

#### 4. Conclusions

A computational scheme that couples a microstructure evolution model and a time-stepping finite element method capable of tracking phase formation is developed in this paper to predict the apparent VE/VP properties of cement paste as a function of time-evolving

microstructures. From the model simulations, the apparent VE/VP behavior of hydrating cement paste due to dissolution of cement grains is a significant factor in the overall early-age creep and relaxation of the paste. The main reasons behind this are the stress transmission from dissolved load bearing phases to surrounding hydrated phases or cement grains, and the generation of apparent strain in the new components that form in deformed configurations (i.e., the newly formed phases have a deformation gradient but no stress). Simulation results also indicate that intrinsic C-S-H viscoelasticity is not likely the primary mechanism leading to the early-age creep and relaxation behavior of cementitious materials; this is because significant C-S-H relaxation results in simulated macroscopic behavior that is in conflict with experimental evidence of early-age aging effects.

The comparison between the evolution of stresses within hydration products predicted by the new computational scheme and that predicted by the solidification theory indicates that the specific assumption made about the extent to which unhydrated phases can transmit stress is key to interpreting VE/VP mechanisms of cement paste. If one stipulates that unhydrated phases do not carry stress (as with the solidification theory), then increased formation of C-S-H can lead to aging of VE/VP properties of cement paste (e.g., reductions in creep or relaxation rates at later ages). However, as demonstrated by the new computational scheme and model presented herein, if one presumes that unhydrated phases may transmit stress once the solid phases form a percolated network, then their dissolution results in an increase in stress on hydration products as hydration progresses. This increase in stress in the less stiff hydration products results in a greater relaxation rate, counteracting any reduction in rate due to the increased formation of C-S-H does not act as a source of aging of VE/VP properties of cement paste. Conversely, the slowing of the cement

dissolution process (associated with the hydration reaction) with time may lead to lower creep and relaxation rates of cement paste at later ages, contributing strongly to the early age aging of cement paste.

The model discussed in this paper is yet unable to fully explain certain observed VE/VP behavior of cement paste, including overall observed magnitude and differences between responses associated with tensile and compressive stresses. Thus, additional mechanisms must be considered in addition to hydration induced cement grain dissolution.

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