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Modeling Shrinkage of Portland Cement Paste

by Feng Lin and Christian Meyer

A multi-scale constitutive model that simulates the shrinkage of hardening cement paste is developed based on the theories of poromechanics and mechanics of composites. Capillary stress is considered the driving force of autogenous shrinkage. The applied pressure, which can be another driving force of shrinkage for some applications, is also considered in the model. A multi-scale and micromechanical model for the elastic properties of hardening cement paste is first formulated; the nonlinearity and creep behaviors of calcium-silicate-hydrate (C-S-H), which are of great importance for the shrinkage of cement paste, are then considered in the model. The time-dependent properties of C-S-H are back-calibrated against the experimental results for autogenous shrinkage of cement paste. The model is finally verified by reproducing the elastic properties as well as the autogenous shrinkage of different cement pastes, and the results are compared with other experimental data.

Keywords: cement paste; composites; creep; elastic moduli; micromechanical model; poromechanics; shrinkage.

INTRODUCTION

The importance of shrinkage calls for concerted research efforts in modeling shrinkage of portland cement paste. Limited models with different levels of complexity and applicability can be found in the literature of the past several decades. From a material property point of view, they can be categorized in two families: 1) the macro or phenomenological models, which regard cement paste as one macromaterial and assign it a single set of material properties such as elastic moduli[1-5]; and the micromechanical ones, which consider the microstructure and/or the constituent components of cement paste.[6-11] The first group of models is relatively simple, but the material constants required for such models usually do not have clear physical meanings and are difficult to obtain. The second group of models, although more logical in their formulation, are usually very sophisticated and their degrees of validity depend on the clear understanding and reasonable assumptions of the microstructure and constituent components of cement paste. Numerical analysis such as the finite element method was used in some of these models to obtain the shrinkage[6,8] or the effective elastic moduli[12] of hardening cement paste. Therefore, it is likely to be too involved for practical applications. Mabrouk et al.[10] employed the solidification theory proposed by Bažant and Prasannan[13] to analyze the shrinkage of young concrete considering the time-dependent properties of the cement matrix. The solidification theory,[13] however, is not adequately accurate for modeling cement paste due to the very complex components and microstructure at the scale of cement matrix.[14] Some models are based on the mechanics of composite materials,[7,9,11] which could address the composite characteristics of cement paste yet remain simple enough for practical applications. The available micromechanical models, however, usually do not adequately take into account the fact that cement paste is fundamentally a porous medium.[14] Its time-dependent properties are not properly considered either. Moreover, the identification of model parameters for most of these models is not straightforward, making them difficult to apply.

A multi-scale, micromechanics-based constitutive model was developed in this study that aimed at describing the average shrinkage properties of a representative volume of portland cement paste and could be embedded in numerical analysis frameworks for practical problems, such as the finite element analysis. The shrinkage model assumed that the relative humidity (RH) was high (that is, RH > 70%), which is relevant for cement pastes under sealed curing condition, or with small amount of moisture loss due to external drying. With high relative humidity, capillary stress could be considered to be the principal driving force of autogeneous shrinkage. The mechanical framework of this constitutive model, however, was such that it could be used to simulate shrinkage of cement paste at low relative humidity as well.

RESEARCH SIGNIFICANCE

Modern concrete materials science has been maturing slowly to the point where it is now possible to compute various properties of cement composites using only basic principles and the material properties of the constituent components. Most models used for these purposes, however, generally require vast computational efforts. The study presented herein points a way to avoid such extensive computations by effectively combining the theories of poromechanics and mechanics of composites.

DRIVING FORCES OF SHRINKAGE

To determine the volume changes of cement paste (a porous medium), the driving forces need to be identified. These can be divided into two categories: the applied pressure that is easy to quantify, and the internal load—the driving force of autogenous shrinkage and/or drying shrinkage—which is more difficult to identify.

Accompanying the reduction of water in capillary pores due to chemical shrinkage and drying or desiccation of cement paste, solid surface tension, disjoining pressure, and capillary stress may take effect, resulting in the shrinkage of cement paste as a function of the internal relative humidity in the capillary pores. Surface tension,[3] capillary stress,[2,4,5,8] and empirical relations[9,10] have all been used as the internal load to calculate autogenous shrinkage of cement-based materials. Solid surface tension is relevant for shrinkage of cement paste at low relative humidity (that is, RH < 40%), whereas disjoining pressure and capillary stress play major roles at high relative humidity, which is the main concern of

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the present study.[2] The quantification of disjoining pressure, however, is difficult, and how it induces shrinkage of cement paste is not clearly understood. Therefore, capillary stress, which γ can be conveniently determined with relative humidity, is assumed to be the main driving force of shrinkage in the model presented herein.

Capillary stress p_c can be related to the pore size of cement paste through the Young-Laplace equation, $p_c = 4\gamma/\varphi_{pore\text{-}water}$, in which γ is the surface tension of water, which equals 0.07197 N/m (4.109 × 10^{-4} lb/in.); and $\varphi_{pore\text{-}water}$ is the diameter of the largest water-filled capillary pore, which is related to the degree of hydration, the water-cement ratio (w/c), and the fineness of cement. An equation was proposed by Lin[15] to predict $\varphi_{pore\text{-}water}$.

MODEL FORMULATION

A rational constitutive model of autogenous shrinkage of hardening cement paste should take into account the thermo-chemo-mechanical reactions, relations, and properties of its constituent components. At the same time, the model should be relatively simple so that it can be applied to analyze practical problems. In particular, the material constants of the model should have clear physical meaning and be easy to calibrate. Cement paste can be regarded as a composite medium because of its constituent components, and it is fundamentally a porous medium as well[14]; therefore, mechanics of composites and poromechanics[16] can serve as the theoretical bases for the constitutive model. Bernard et al.[17] and Ulm et al.[14] demonstrated that the salient elastic properties of hardened cement paste could be captured by combining the two theories. There is still a long way to go, however, before their theory can be used to develop a rational autogenous shrinkage model for hardening cement paste. First, anhydrous cement was excluded, which can be an important constituent of hardened cement paste; second, the time-dependent material properties were not taken into account; and third, the poromechanics issue of Biot's coefficient for early-aged cement paste was not resolved. Biot's coefficient is defined as $b = 1 - (K^d/K^s)$, in which K^d and K^s are the bulk moduli of the porous medium and the solid phase of porous medium, respectively. For hydrating cement paste, because the capillary porosity and the bulk moduli of both the porous medium and the solid phase are changing constantly, b should also change accordingly, and it is affected by the time-dependent properties of C-S-H as well.

In the present study, a new constitutive model is presented in two steps. First, considering the aging effects on hardening cement paste, its elastic properties are modeled using a concept similar to the solidification theory,[13] then a shrinkage model for cement paste is presented that considers the time-dependent properties of C-S-H.

Modeling effective elastic properties of cement paste

Elastic properties of constituent components of cement paste—The constituent components of cement paste include hydration products (mainly C-S-H and CH), pores of different sizes, pore water, and anhydrous cement. Based on the available experimental observations, the anhydrous cement is surrounded by hydration products, that is, the anhydrous cement forms the core of the solid phase of cement paste and the hydration products form the shell around it.[8] The hydration products may also include calcium sulfoaluminate hydrate (mainly ettringite $C_6A\overline{S}_3H_{32}$ and/or monosulfoaluminate $C_4A\overline{S}H_{12}$) and others, but their elastic moduli are close to those of C-S-H.[12] Therefore, C-S-H and CH are considered herein to be the only hydration products. Nielsen proposed a mesomechanical constitutive model.[18,19] The elastic properties of the four major clinker phases (namely, C_3S, C_2S, C_3A, and C_4AF) of anhydrous cement have been investigated extensively,[20-22] for example, by nanoindentation. The average values obtained by Acker[21] and Velez et al.[22] are used herein as the mean effective elastic moduli of anhydrous cement. Other investigators have also determined the elastic moduli of C-S-H using nanoindentation.[23-25] The two types of C-S-H, namely, low-density and high-density C-S-H, have Young's moduli that are quite similar (21.7 and 29.4 GPa [3147 and 4264 ksi], respectively[25]). Therefore, single values of elastic moduli are assigned to C-S-H in this study, adopting the values calculated by Constantinides and Ulm[25] for a cement paste with a w/c of 0.5. It should be noted that the elastic moduli measured by nanoindentation are the so-called drained ones,[14] indicating that the elastic moduli can be obtained in an isothermal test with the pore fluid free to flow. In contrast, if the pore fluid is not allowed to flow, the elastic moduli should be considered undrained. The relation between the drained bulk modulus and the undrained one can be derived by poromechanics.[16] The undrained elastic moduli calculated by Ulm et al.[14] for the aforementioned cement paste are adopted herein, and the bulk modulus of pore water is set to 2.2 GPa (319 ksi).[26] For the elastic moduli of CH, the values measured by Monteiro and Chang[27] are used. The aforementioned elastic properties of the constituent components of cement paste are listed in Table 1. Although different investigations may determine different specific values, those of Table 1 are considered the intrinsic properties of the constituent components of cement paste, independent of the cement type, w/c, and curing conditions.

Micromechanical model for effective elastic properties of cement paste—Cement paste can be considered a composite medium, for which the characteristics of the different constituent components should be investigated at different length scales.[14] Anhydrous cement should be included because it is also an important constituent component. Thus, using different length scales, four levels of composite media can be identified for cement paste. Starting from the

Table 1—Elastic properties of constituent components of cement paste

Elastic moduli	Clinker	C-S-H		CH	Pore water
		Drained	Undrained		
Bulk modulus K	113.0 GPa (16,389 ksi)	15.2 GPa (2205 ksi)	18.3 GPa (2654 ksi)	40.0 GPa (5802 ksi)	2.2 GPa (319 ksi)
Shear modulus G	53.6 GPa (7774 ksi)	9.6 GPa (1392 ksi)		16.0 GPa (2321 ksi)	—

smallest scale, they are C-S-H matrix (Level 0), hydration products (Level I), solid phase of cement paste (Level II), and cement paste (Level III). The C-S-H matrix (Level 0) is treated similarly herein as CH and the anhydrous cement, but with drained or undrained elastic moduli. Hydration products (Level I) are assumed to consist of the C-S-H matrix and the CH inclusions. Solid phase of cement paste (Level II) consists of hydration products and anhydrous cement. Finally, cement paste (Level III) consists of the solid phase of cement paste and capillary pores. Therefore, only three levels of composite media are considered herein. The effective elastic moduli of a specific level are used as the input for the next higher level, treating the lower level composite as one effective medium, which is called the up-scale approach. The three levels of composites are now discussed in some detail.

Hydration products (Level I) are assumed to consist of the C-S-H matrix and the CH inclusions. The volume ratios of C-S-H and CH in hydration products can be calculated from the chemical composition of cement.[14,28] The volume fraction of CH is generally much smaller than that of C-S-H. Therefore, CH can be treated as randomly distributed inclusions with a small volume fraction embedded in the C-S-H matrix. The effective medium theory of Mori and Tanaka[29] is ideal for such a composite. The shape of the CH inclusions and the way they are distributed in the C-S-H matrix are difficult to define, but because their volume fraction is small, it is further assumed that the CH inclusions are spherical and dispersed isotropically within the C-S-H matrix. With these assumptions, the effective bulk and shear moduli of hydration products, K_{hp} and G_{hp}, can be obtained as[30]

$$K_{hp} = K_{CSH} + \frac{f_{CH}(K_{CH} - K_{CSH})K_{CSH}}{(1 - f_{CH})(K_{CH} - K_{CSH})\alpha_1 + K_{CSH}} \tag{1}$$

$$G_{hp} = G_{CSH} + \frac{f_{CH}(G_{CH} - G_{CSH})G_{CSH}}{(1 - f_{CH})(G_{CH} - G_{CSH})\alpha_2 + G_{CSH}} \tag{2}$$

with $\alpha_1 = \dfrac{3K_{CSH}}{3K_{CSH} + 4G_{CSH}}$ and $\alpha_2 = \dfrac{6(K_{CSH} + 2G_{CSH})}{5(3K_{CSH} + 4G_{CSH})}$.

Based on stoichiometry of the hydration reactions of the two calcium silicates, C_3S and C_2S, given the gram molecular weight (GMW) and density ρ of each reactant and product,[24,31] the volume fraction of CH inclusions in the hydration products, f_{CH}, can be estimated as

$$f_{CH} = \frac{0.19p_{C_3S} + 0.06p_{C_2S}}{0.69p_{C_3S} + 0.72p_{C_2S} + V_{others}} \tag{3}$$

where p_{C_3S} and p_{C_2S} are the Bogue mass fractions of C_3S and C_2S, respectively; V_{others} is the volume of the hydration products other than C-S-H and CH, such as $C_6A\bar{S}_3H_{32}$ and $C_4A\bar{S}H_{12}$.

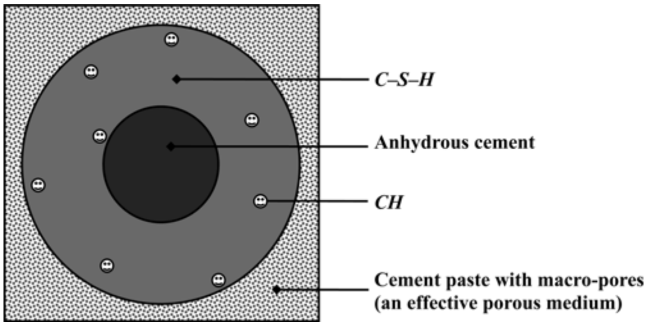

Fig. 1—Micromechanical model for hardened cement paste.

If the degree of hydration is less than 1.0, anhydrous cement will also exist. As shown in Fig. 1, an anhydrous cement particle is assumed to be spherical in shape surrounded by a shell consisting of hydration products, and they together form the solid phase of cement paste (Level II). According to Powers and Brownyard,[32] the volume fraction of the anhydrous cement inclusions in the solid phase of cement paste is

$$f_{ace} = \frac{0.32(1 - \alpha)}{0.32(1 - \alpha) + 2.2 \times 0.32\alpha} = \frac{1 - \alpha}{1 + 1.2\alpha} \tag{4}$$

where α equals the degree of hydration. The composite sphere can now be considered as being surrounded by some isotropic effective medium containing macropores, pore water, and the solid phases similar to the composite sphere, as shown in Fig. 1, which is identical to the three-phase (or the generalized self-consistent scheme) model[33,34] if the hydration products are considered to be one effective medium. According to Christensen,[34] the effective bulk modulus of the solid phase of cement paste (Level II) can be expressed as

$$K_{ces} = K_{hp} + \frac{f_{ace}(K_{ace} - K_{hp})(3K_{hp} + 4G_{hp})}{3K_{ace} + 4G_{hp} - 3f_{ace}(K_{ace} - K_{hp})} \tag{5}$$

in which K_{ace} is the bulk modulus of the anhydrous cement clinker given in Table 1. The effective shear modulus can be obtained by solving the following quadratic equation[34]

$$A_1\left(\frac{G_{ces}}{G_{hp}}\right)^2 + 2A_2\left(\frac{G_{ces}}{G_{hp}}\right) + A_3 = 0 \tag{6}$$

where the coefficients A_1, A_2, and A_3 are functions of the elastic properties of the hydration products and the anhydrous cement as well as the volume fraction of the anhydrous cement.[34] The solution of Eq. (6) yields two values of G_{ces}. The correct value of G_{ces}, however, can be identified by observing that it cannot be negative and is usually smaller than the effective bulk modulus. The second condition assumes that Poisson's ratio of the solid phase is larger than 1/8, the validity of which still needs to be verified by experiments.

Finally, the effective drained bulk modulus and shear modulus of cement paste (Level III) are obtained using the self-consistent scheme by solving the following nonlinear equations[30,33]

$$K^d_{cep} = K_{ces} - \phi K_{ces}\frac{3K^d_{cep} + 4G_{cep}}{4G_{cep}} \tag{7}$$

$$G_{cep} = G_{ces} - \phi G_{ces}\frac{15(1-\nu_{cep}^{d})}{7-5\nu_{cep}^{d}} \tag{8}$$

where ν_{cep}^{d} is the effective drained Poisson's ratio of cement paste, and ϕ is the capillary porosity. If the external shrinkage can be neglected, for example, for a cement paste cured under a saturated condition, according to Powers and Brownyard[32]

$$\phi = \frac{0.0625\alpha}{0.32+\frac{w}{c}} + \frac{1.0}{0.32+\frac{w}{c}}\left(\frac{w}{c} - 0.4\alpha\right) = \frac{\frac{w}{c} - 0.3375\alpha}{0.32+\frac{w}{c}} \tag{9}$$

Gel pores are not considered on this level. They are assumed to be integral components of the C-S-H matrix. The effective elastic moduli of C-S-H given in Table 1 already account for the effects of gel pores.

The self-consistent scheme, however, encounters problems when the capillary porosity is very large, in which case the effective shear modulus of a composite medium with void inclusions and incompressible matrix can be obtained directly as[33]

$$G = \frac{3(1-2f_{void})}{3-f_{void}}G_m \tag{10}$$

with f_{void} being the volume fraction of voids. It can be seen from Eq. (10) that when $f_{void} \geq 0.5$, the self-consistent scheme predicts a zero or even negative shear modulus. The same problem exists for an effective medium with a compressible matrix, such as the cement paste at early age. This is reasonable because stiffness of cement paste can only develop at a certain degree of hydration when the originally separated cement particles form a solid skeleton of hydration products.[8] This process is known as percolation and the degree of hydration at which the cement paste is percolated (set) depends on the *w/c*, or the void ratio of cement paste.[35,36] Therefore, the time when the stiffness simulated via the self-consistent scheme becomes positive is assumed to be the time of setting.

Consideration of aging effect on mechanical properties of hydration products

During cement hydration, the hydration products exhibit considerable inelastic behavior under large and/or sustained loading, and the mechanical properties, especially the time-dependent ones, are likely to change with age. Therefore, an approach that is more logical than Eq. (4) to (6) should be followed to model the mechanical properties of hardening cement paste. In this study, an approach that is similar to the solidification theory[13] is employed considering the following case: at time t, the degree of hydration is α; after a certain time step Δt, the degree of hydration becomes $\alpha + \Delta\alpha$. The volume of the anhydrous cement consumed during Δt is ΔV. If Δt is sufficiently small, the newly formed hydration products can be assumed to exhibit the same mechanical properties as the previously formed ones. Using the aforementioned model for Level II, the newly formed hydration products may exist either inside or outside of the previously formed hydration products, or both. Because the volume of the newly formed hydration products is approximately 2.2 times larger than the consumed anhydrous cement, that is, $2.2\Delta V$, they should be created both inside and outside of the previously formed hydration products, as shown in Fig. 2. It is assumed that the fraction ΔV is formed inside and the remaining fraction $1.2\Delta V$ outside. It is also noted that a similar mechanism was discussed by Brunauer et al.[37]

The effective mechanical properties of the solid phase at time $t + \Delta t$ can now be obtained via the following three steps (Fig. 3): first, the effective mechanical properties of the anhydrous cement core and the inner layer of the newly formed hydration products are determined using the three-phase model; in the second step, the previously formed hydration products serve as the matrix medium in the three-phase model, and the effective mechanical properties obtained from the previous step are taken as those of a new core consisting of anhydrous cement and the inner layer of the newly formed hydration products; finally, the three-phase model is used again to obtain the effective mechanical

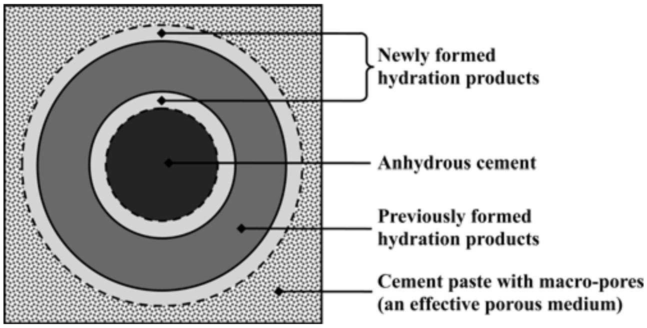

Fig. 2—Micromechanical model for hardening cement paste.

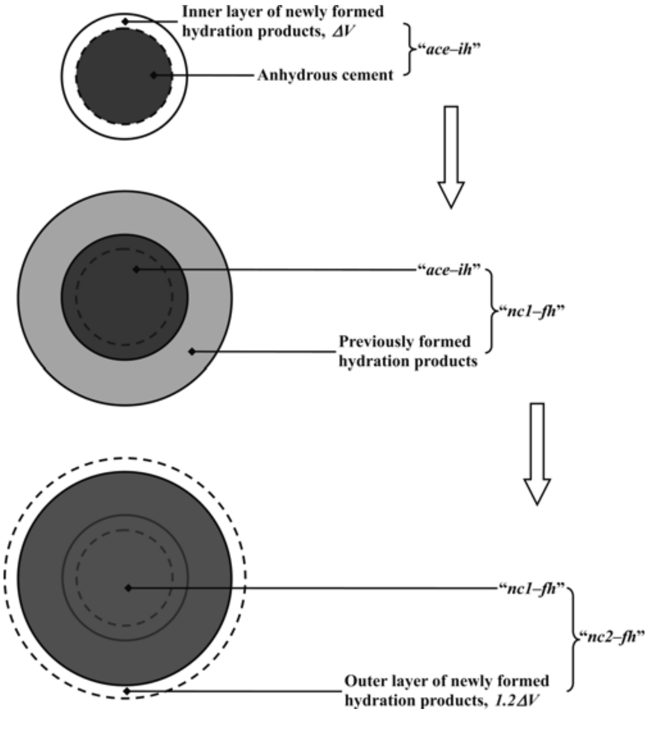

Fig. 3—Illustrated procedure of simulating effective mechanical properties of solid phase of hardening cement paste at time t + Δt.

properties of the solid phase at time $t + \Delta t$, treating the outer layer of the newly formed hydration products as the matrix medium and the effective medium enclosed by it as the inclusion. For example, similar to Eq. (5), the effective bulk modulus of the solid phase at time $t + \Delta t$ can be obtained via the following expressions

$$K_{ace-ih} = K_{ih} + \frac{f_{ace-ih}(K_{ace} - K_{ih})(3K_{ih} + 4G_{ih})}{3K_{ace} + 4G_{ih} - 3f_{ace-ih}(K_{ace} - K_{ih})} \quad (11)$$

$$K_{nc1-fh} = K_{fh} + \frac{f_{nc1-fh}(K_{ace-ih} - K_{fh})(3K_{fh} + 4G_{fh})}{3K_{ace-ih} + 4G_{fh} - 3f_{nc1-fh}(K_{ace-ih} - K_{fh})} \quad (12)$$

$$K_{nc2-oh} = K_{oh} + \frac{f_{nc2-oh}(K_{nc1-fh} - K_{oh})(3K_{oh} + 4G_{oh})}{3K_{nc1-fh} + 4G_{oh} - 3f_{nc2-oh}(K_{nc1-fh} - K_{oh})} \quad (13)$$

with the subscripts *fh* denoting the previously formed hydration products; *ih* and *oh* denoting the inner and outer layer of the newly formed hydration products, respectively; *ace-ih* denoting the core formed by anhydrous cement and the inner layer of the newly formed hydration products; *nc*1-*fh* denoting the core formed by anhydrous cement, the inner layer of the newly formed hydration products and the previously formed hydration products; and *nc*2-*oh* denoting the solid phase of cement paste. The corresponding effective shear moduli can be obtained using equations similar to Eq. (6), with the parameters changed correspondingly.

The aforementioned procedure can be repeated when more layers of hydration products are formed. Using this approach, the aging effect on the mechanical properties of hydration products can also be considered. The linear elastic properties predicted by this procedure are the same as those calculated using Eq. (4) to (6).

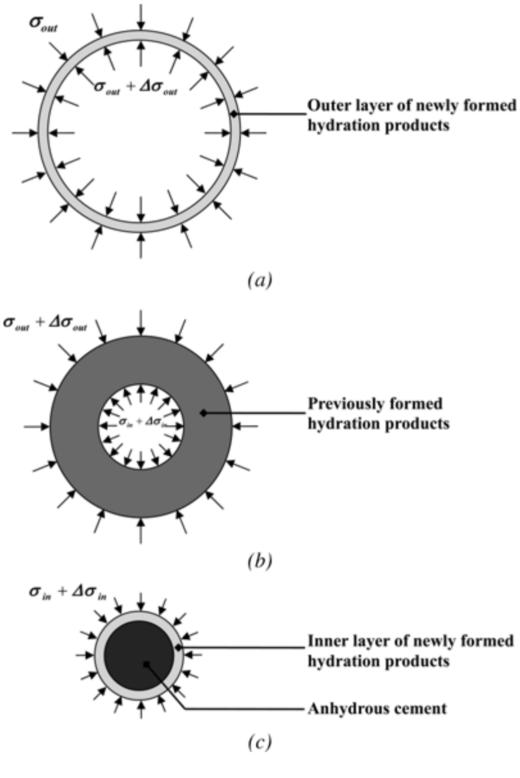

Fig. 4—Illustration of stress redistribution in solid phase of cement paste.

Modeling shrinkage of hardening cement paste

To model the shrinkage of hardening cement paste, it is assumed that the multi-scale and micromechanical framework used to simulate the effective elastic properties of cement paste is still valid when nonlinearity and creep are taken into account. The following equation for the differential volumetric strain of nonlinear elastic porous media can be used to calculate the volume change of cement paste[16]

$$d\varepsilon_v = \frac{d\sigma_b + bS_w dp_c}{K^d} \quad (14)$$

where ε_v is the volumetric strain, σ_b is the bulk stress of the porous medium, b is the Biot's coefficient, S_w is the saturation ratio of pores, p_c is the capillary stress, and K^d is the drained bulk modulus.

Consideration of nonlinearity and stress redistribution in micromechanical model

Herve and Zaoui[38] used the three-phase model to describe the nonlinearity of matrix-inclusion composites by replacing the constant elastic moduli of the constituent components with the tangent moduli. This approach is applied to the modeling schemes at different levels of composites, that is, the Mori-Tanaka scheme at Level I, the three-phase model scheme at Level II, and the self-consistent scheme at Level III, by replacing the constant moduli in Eq. (1) to (2), (11) to (13), and (7) to (9) with the corresponding tangent moduli. Here, only the C-S-H matrix is considered to be nonlinear, whereas the anhydrous cement and CH are still assumed to behave linear elastically, which means that their elastic moduli are constant.

Because the stress level of the C-S-H matrix at different ages certainly influences its nonlinear and creep behavior, the stress redistribution during cement hydration must be determined. Even if the externally applied loads on the solid phase are constant during the time step Δt, the stresses in different layers of hydration products (and hence, in different layers of the C-S-H matrixes) and the anhydrous cement core vary during this time period due to cement hydration. The stress redistribution can be determined by considering both stress equilibrium and deformation compatibility for the composites. According to the model of Fig. 2, an inner and an outer layer of hydration products are formed during Δt. The applied stress on the original anhydrous cement core, which is now the effective stress of the inner layer of the newly formed hydration products and the reduced anhydrous cement core will change due to cement hydration and in turn affect the stress and strain of the previously formed hydration products. The change in the total effective volume of the previously formed hydration products, the inner layer of the newly formed hydration products, and the reduced anhydrous cement core must remain compatible with the deformation of the outer layer of the newly formed hydration products. The resulting stress redistribution in the various layers of hydration products can then be calculated. Because the main concern is the shrinkage of cement paste, only the bulk deformation is considered herein. As shown in Fig. 4, at time t, the effective bulk stresses of the solid phase and the anhydrous cement core are denoted as σ_{out} and σ_{in}, respectively. At time $t + \Delta t$, the applied stress on the solid phase is assumed to be the same as that at time t, and the effective stress of the original volume of solid phase becomes

$\sigma_{out} + \Delta\sigma_{out}$ due to stress redistribution. The effective stress of the inner layer of the newly formed hydration products and the reduced anhydrous cement core (compared with the original anhydrous cement core) becomes $\sigma_{in} + \Delta\sigma_{in}$. The change in the effective bulk strain of the inner layer of the newly formed hydration products and the reduced anhydrous cement core, $\Delta\varepsilon_{in}$, causes the variation in strain of the solid phase, which can be calculated using the three-phase model[30]

$$\Delta\varepsilon_{out} = \frac{\Delta\varepsilon_{in}[f_{in}(g-1)+1]}{g} \tag{15}$$

$$g = \frac{3K^t_{hp} + 4G^t_{hp}}{3K^t_{in} + 4G^t_{hp}} \tag{16}$$

in which K^t_{hp} and G^t_{hp} are the tangent bulk and shear moduli of the previously formed hydration products, respectively. K^t_{in}, the tangent bulk modulus of the composite volume that was originally the anhydrous cement, can be obtained as

$$K^t_{in} = \frac{\Delta\sigma_{in}}{\Delta\varepsilon_{in}} \tag{17}$$

and

$$f_{in} = \frac{V_{ac}}{V_{ac} + V_{hp}} \tag{18}$$

where V_{ac} and V_{hp} are the volume of the original anhydrous cement core and the previously formed hydration products, respectively. The change in strain, $\Delta\varepsilon_{in}$, can be obtained using the stress $\sigma_{in} + \Delta\sigma_{in}$ and the effective bulk modulus of the composite shown in Fig. 4(c)) as well as the original stress σ_{in} and the bulk modulus of the anhydrous cement. With $\Delta\varepsilon_{in}$ and $\Delta\sigma_{in}$ known, K^t_{in} is readily obtained from Eq. (17). Because the previously formed hydration products contain layers of different ages, the aforementioned procedure usually has to be completed using iteration.

At the same time, the effective volume change should remain compatible with the deformation of the outer layer of the newly formed hydration products, which can be assumed as a spherical shell subject to both an inner pressure $\sigma_{out} + \Delta\sigma_{out}$ and an outer pressure σ_{out}. The volume change of such a spherical shell, according to solid mechanics, can be calculated via

$$\Delta\varepsilon'_{out} = 1.0 - \left[1.0 - \frac{(\beta_3 + \beta_4)}{f_{in} - 1.0}\right]^3 \tag{19}$$

$$\text{with } \beta_3 = \frac{(\sigma_{out} + \Delta\sigma_{out})f_{in} - \sigma_{out}}{3K^t_{oh}} \text{ and } \beta_4 = \frac{\Delta\sigma_{out}}{4G^t_{oh}}$$

where K^t_{oh} and G^t_{oh} are the tangent bulk and shear moduli of the outer layer of the newly formed hydration products, respectively. Because $\Delta\sigma_{in}$ is unknown in advance, the aforementioned calculation procedure should be accomplished iteratively, with the convergence criterion being

$$\left|\frac{\Delta\varepsilon'_{out} - \Delta\varepsilon_{out}}{\Delta\varepsilon_{out}}\right| \le Tol. \tag{20}$$

After the changes in stress of different constituent components due to stress redistribution are obtained, they can be combined with the stress variation due to any change in the external loads during Δt to calculate the corresponding effective strain variations of cement paste. It should be noted that the strain calculated using the aforementioned procedure must be the same as that calculated using the micromechanical model of the previous section if the mechanical properties of all the constituent components of cement paste are linear elastic.

Modeling time-dependent behavior of C-S-H matrix

It is assumed that the bulk strain rate of the C-S-H matrix can be expressed as

$$\dot{\varepsilon}_{CSH} = \dot{\varepsilon}^e_{CSH} + \dot{\varepsilon}^{cr}_{CSH} \tag{21}$$

where $\dot{\varepsilon}^{cr}_{CSH}$ is the creep bulk strain rate, and $\dot{\varepsilon}^e_{CSH}$ is the instant elastic bulk strain rate defined by

$$\dot{\varepsilon}^e_{CSH} = \frac{d\sigma_{CSH}}{K^u_{CSH}\, dt} \tag{22}$$

where $d\sigma_{CSH}$ is the bulk stress increment during time interval dt, which may result from stress redistribution as well as any change in the external loads, and can be calculated via the previously discussed procedure. The stress-averaging scheme in mechanics of composite materials is used in calculating $d\sigma_{CSH}$ with the ratios of different fractions.[34] The undrained bulk modulus of the C-S-H matrix, K^u_{CSH}, should be used to calculate the instant strain increment since the corresponding response of the saturated porous C-S-H matrix is conceptually undrained. The time-dependent properties of C-S-H depend on the stress level, deformation history, and loading rate. Because the stress of a certain layer of the C-S-H matrix varies continuously, the frequently used empirical creep equations are not suitable herein because they usually require storing the entire stress history. In this model, the over-stress viscoplasticity theory proposed by Perzyna[39] is applied. It has the advantage that only the present stress and strain levels are required, which considerably simplifies the model formulation. The creep strain rate thus can be defined as

$$\dot{\varepsilon}^{cr}_{CSH} = \frac{1}{\eta}(\sigma_{CSH} - \sigma_{st})^{n_1} \tag{23}$$

where η and n_1 are the viscous model parameters, and σ_{st} denotes a threshold stress level for the viscous behavior of C-S-H to occur. When σ_{CSH} approaches σ_{st}, the creep strain rate $\dot{\varepsilon}^{cr}_{CSH}$ tends to vanish; and for $\sigma_{CSH} < \sigma_{st}$, $\dot{\varepsilon}^{cr}_{CSH} = 0$; σ_{st} is assumed to be a function of strain, which is expressed as

$$\sigma_{st} = \begin{cases} \dfrac{K_{st}}{b_1}\exp(b_1\varepsilon_{CSH}) - \dfrac{K_{st}}{b_1}, & b_1 \neq 0 \\ K_{st}\varepsilon_{CSH}, & b_1 = 0 \end{cases} \tag{24}$$

where K_{st} and b_1 are model parameters. The slope of the curve relating σ_{st} and ε_{CSH} defined by Eq. (24) increases or decreases, depending on the sign of parameter b_1. The strain increment in the C-S-H matrix during dt can be expressed as

$$d\varepsilon_{CSH} = (\dot{\varepsilon}^{e}_{CSH} + \dot{\varepsilon}^{cr}_{CSH})dt \tag{25}$$

and the tangent bulk modulus of C-S-H at time t as

$$K^{t}_{CSH} = \frac{K^{u}_{CSH}K^{cr}_{CSH}}{K^{u}_{CSH} + K^{cr}_{CSH}} \tag{26}$$

in which K^{cr}_{CSH} is the tangent creep bulk modulus of C-S-H at time t that reads

$$K^{cr}_{CSH} = \frac{d\sigma_{CSH}}{\dot{\varepsilon}^{cr}_{CSH}\,dt} \tag{27}$$

The tangent shear modulus can be obtained by assuming constant Poisson's ratio for the C-S-H matrix, meaning that

$$G^{t}_{CSH} = \frac{G_{CSH}}{K^{u}_{CSH}}K^{t}_{CSH} \tag{28}$$

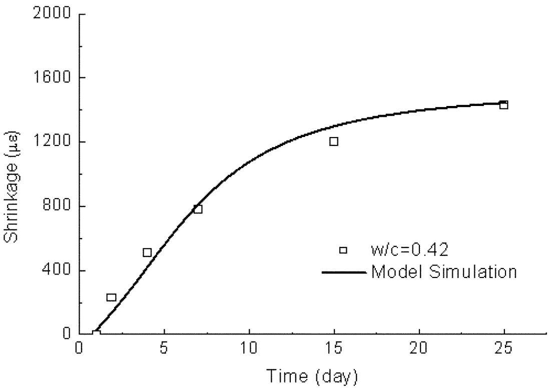

Fig. 5—Simulated and measured autogenous shrinkage of hardening cement paste (experimental data from Hua et al.[8]).

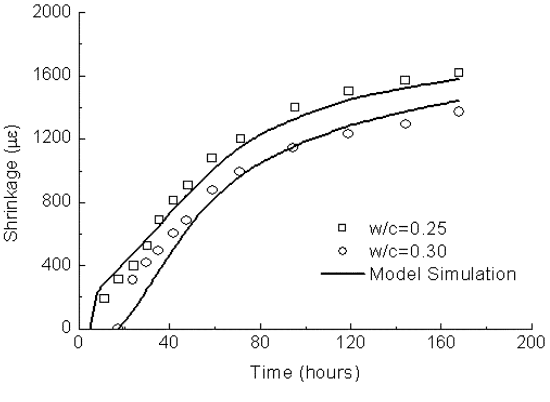

Fig. 6—Simulated and measured autogenous shrinkage of hardening cement pastes (experimental data from Horita and Nawa[40]).

MODEL CALIBRATION

The input parameters for the model include the elastic moduli of the constituent components of Table 1; the capillary porosity ϕ, which may be obtained from Eq. (9) and using the data of external shrinkage of cement paste during its hydration; the volume fraction of CH in the hydration products, f_{CH}, which can be estimated with Eq. (3); the degree of hydration α, which can be obtained through experiments; and the four time-dependent parameters, η, n_1, K_{st}, and b_1, which should be intrinsic properties of the C-S-H matrix that do not vary for different cements. Because the creep deformation of cement paste is assumed to arise from the time-dependent deformation of C-S-H only, it is possible to back-calibrate these time-dependent parameters against the experimental data on the volume change of cement paste. Furthermore, for the obtained material parameters to represent the intrinsic properties of C-S-H as well as possible, details of the hydration kinetics and capillary stress developments must also be provided for a specific cement paste tested. Unfortunately, very few available experimental data provide such comprehensive information. Three useful sets of experimental data are identified and used to calibrate the parameters.[5,8,40] The changes in relative humidity (RH) reported by Horita and Nawa[40] and Lura et al.[5] can be converted to capillary stresses p_c via the Kelvin Equation

$$\ln(\text{RH}) = \frac{-p_c V_m}{RT} \tag{29}$$

where T is the absolute temperature; V_m is the molar volume of the pore solution, which in the case of this study equals 18×10^{-6} m^3/mol (1.1 in.^{3}/mol); and R is the universal gas constant that is 8.314 J/(mol·K) [73.585 in.·lb/(mol·K)]. Due to salt solution in the pore liquid, however, the measured RH is lower than that representing the meniscus radius in cement paste. Therefore, the reported changes in RH are corrected using the method of Lura et al.[5] The drop of RH is corrected to start at 100%. The difference between the measured RH at the moment of RH dropping and 100% is assumed to be constant throughout the RH development. The hydration kinetics of the experiments by Horita and Nawa[40] is obtained from the reported ratios of combined water according to Powers' theory.[32]

At the beginning of hydration, cement paste may exhibit expansion due to the formation of ettringite and other mechanisms,[41] which is not considered herein. The volume change before set is not taken into account either, because such behavior cannot be described within the framework of solid mechanics. As a matter of fact, any chemical shrinkage or expansion during that period would appear as external volume change and require no constitutive model for quantification. Therefore, any measured autogenous shrinkage is set to zero at the time when cement paste shrinks, or sets, or RH drops—whatever occurs last. The comparisons between the simulated and the measured shrinkage also start at that moment. The predictions of shrinkage presented in the next section follow this principle as well. Comparisons of the simulated autogenous shrinkage with experimental data are shown in Fig. 5 to 7 for the three sets of tests. The single set of time-dependent material constants of C-S-H given in Table 2 is used for all these cement pastes. The volume ratios of CH in the hydration products obtained by Eq. (3) and the provided chemical cement composition are all approximately 0.2 for the three cements. The shrinkage presented herein refers to the volumetric shrinkage instead of the linear shrinkage reported in some references. They are related by a factor of 3. Also, for autogenous shrinkage, capillary stress p_c is the only driving force according to Eq. (14), with the applied stress σ_b being 0. It should be pointed out that the time-dependent parameters of Table 2 are based on rather limited experimental data and need to be further verified against more test results.

MODEL VERIFICATION

Verifying model for effective elastic properties of cement paste

The model reproductions of elastic moduli of the D cement pastes at an age of 56 days with different *w/c* are compared with the experimental data of Haecker et al.[12] in Fig. 8. The elastic moduli of Table 1 are used as inputs for the different cement pastes. The elastic moduli reported by Haecker et al.[12] were measured using elastic resonance tests, which should be considered undrained. Therefore, the undrained bulk modulus for C-S-H matrix of Table 1 is used in Eq. (1) to (2) to calculate the effective elastic moduli of hydration products. The measured degree of hydration is treated as an input for the D cement pastes.[12] The volume fraction of CH provided in the same reference is also used. To avoid the error introduced by ignoring the external shrinkage of cement paste of Eq. (9), the capillary porosity simulated by the CEMHYD3D program[36] is adopted to calculate the effective drained elastic moduli in Eq. (7) to (8).

The model is then used to reproduce the elastic moduli of two hardening cement pastes.[20] The comparison of the model reproductions with the experimental data shown in Fig. 9 to 10 is good for the cement paste with *w/c* = 0.4; while for the one with *w/c* = 0.35, the model overestimates the elastic moduli at very early age to some extent, but the results are still acceptable. The discrepancies may partially be attributable to the difficulties of obtaining experimental measurements at very early age of hydration,[12] or to the parameters used for the simulation. In this model, a single set of elastic properties was assigned to the four different clinker phases (for example, C_3S, C_2S, C_3A, and C_4AF), while according to the available experimental results, the specific values of the elastic properties of anhydrous cement may vary with different chemical compositions. This may explain the fact that the model overestimates the experimental results

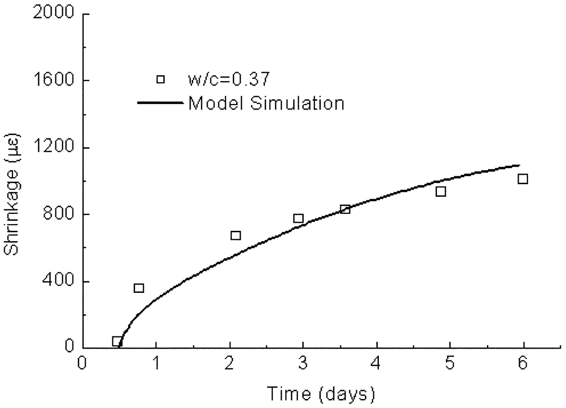

Fig. 7—Simulated and measured autogenous shrinkage of hardening cement paste (experimental data from Lura et al.[5])

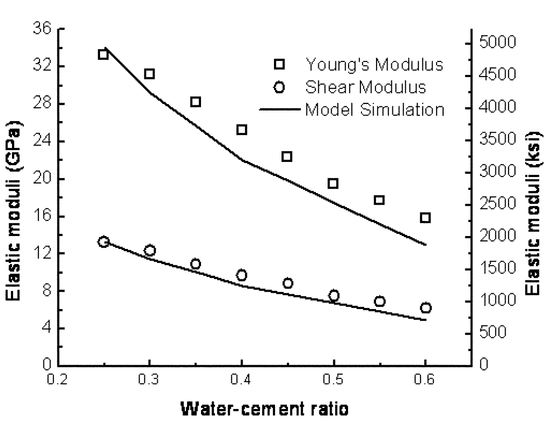

Fig. 8—Reproduced (using capillary porosity simulated by CEMHYD3D) and measured elastic moduli as function of w/c of cement pastes at 56 days (experimental data from Haecker et al.[12]).

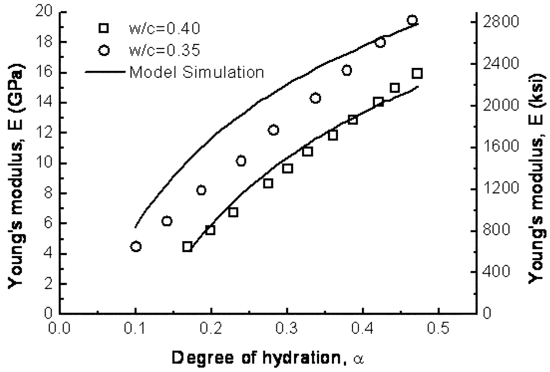

Fig. 9—Reproduced and measured Young's moduli as function of degrees of hydration of cement pastes (experimental data from Boumiz et al.[20]).

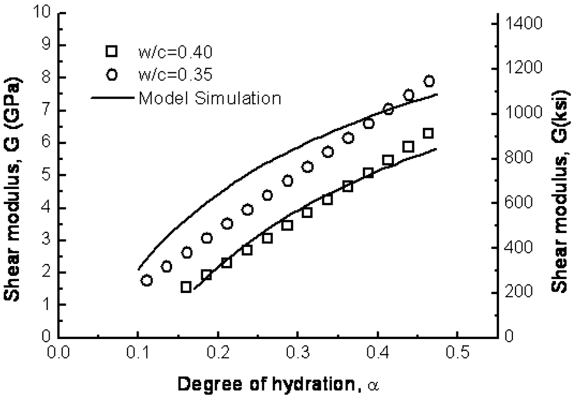

Fig. 10—Reproduced and measured shear moduli as function of degrees of hydration of cement pastes (experimental data from Boumiz et al.[20]).

Table 2—Time-dependent material constants of C-S-H

Material constant	n_1	η	K_{st}	b_1
Value	1.05	7×10^5 (GPa)^{n_1} (1.30×10^8 (ksi)^{n_1})	2800 GPa (4.06×10^5 ksi)	1700

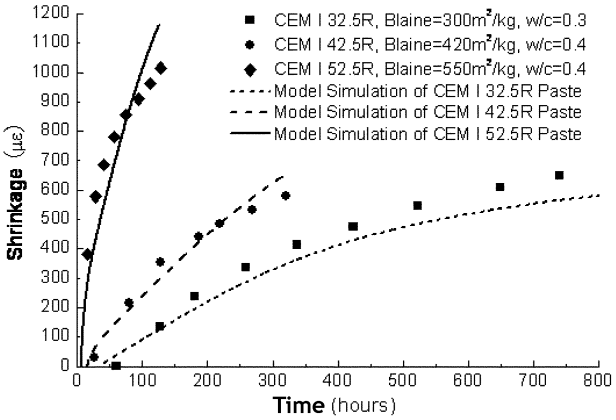

Fig. 11—Reproduced and measured autogenous shrinkage of cement pastes (experimental data from Koenders[42]).

of Boumiz et al.[20] but slightly underestimates those of Haecker et al.[12] The lack of knowledge of external shrinkage may explain the slight underestimations of the model reproductions at later ages in Fig. 9 to 10.

Verifying model for shrinkage of hardening cement paste

In Fig. 11, the predictive capacity is validated by reproducing the experimental results for autogenous shrinkage of cement pastes reported by Koenders.[42] The parameters of Tables 1 and 2 are used as inputs, the fraction of CH is calculated using Eq. (3), and the capillary porosity is obtained through Eq. (9) by considering the accumulative shrinkage. The degrees of hydration and capillary stresses used to calculate the autogenous shrinkage of the three cement pastes are obtained using the hydration kinetics model proposed by Lin.[15] It can be seen that the proposed shrinkage model can successfully predict the autogenous shrinkage of cement paste under ambient conditions.

SUMMARY

A multi-scale and micromechanical constitutive model for predicting the volume changes of hardening portland cement paste has been formulated and validated in this study.

The elastic properties of hardening cement paste were modeled first based on the theories of poromechanics and mechanics of composites. The up-scale approach was adopted in the constitutive modeling, starting from the hydration products that are assumed to be composed of the C-S-H matrix and CH inclusions only, to the solid phase of cement paste that consists of anhydrous cement and hydration products, and finally to the cement paste. To determine the properties of the composite materials, the Mori-Tanaka scheme was used at the scale of hydration products; the three-phase model scheme was applied at the scale of the solid phase of cement paste; and the self-consistent scheme was employed at the scale of cement paste. The increase in volume fraction of hydration products during cement hydration was also considered in the model.

This micromechanical framework was then extended to take into account the effects of nonlinearity and creep. This was accomplished by considering both stress equilibrium and deformation compatibility at the scale of the solid phase of cement paste. A time-dependent constitutive model describing the volume changes of C-S-H based on the over-stress viscoplasticity theory was proposed and incorporated in the micromechanical framework, with the time-dependent model parameters back-calibrated using experimental data on the autogenous shrinkage of cement pastes.

Finally, the model was validated against available experimental data of elastic properties and autogenous shrinkage of different cement pastes, using the intrinsic elastic properties of the main constituent components of cement paste reported in various references as well as the calibrated intrinsic time-dependent properties of C-S-H.

The effects of mineral and chemical admixtures as well as inert fillers can be incorporated into the proposed shrinkage model if the relevant experimental data become available. The application of the proposed constitutive model to predict the volume change of massive cement paste can be attempted by using a numerical procedure such as the finite element method. The proposed multiscale and micromechanical framework used herein can also be applied to model the volume changes of mortar and concrete.

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REFERENCES

1. Paulini, P., "Through Solution Model for Volume Changes of Cement Hydration," *Cement and Concrete Research*, V. 24, No. 3, 1994, pp. 488-496.

2. Hua, C.; Acker, P.; and Ehrlacher, A., "Analyses and Models of the Autogenous Shrinkage of Hardening Cement Paste I. Modelling at Macroscopic Scale," *Cement and Concrete Research*, V. 25, No. 7, 1995, pp. 1457-1468.

3. Koenders, E. A. B., and van Breugel, K., "Numerical Modelling of Autogenous Shrinkage of Hardening Cement Paste," *Cement and Concrete Research*, V. 27, No. 10, 1997, pp. 1489-1499.

4. Shimomura, T., and Maekawa, T., "Analysis of the Drying Shrinkage Behavior of Concrete Using a Micromechanical Model Based on the Microstructures of Concrete," *Magazine of Concrete Research*, V. 49, No. 181, 1997, pp. 303-322.

5. Lura, P.; Jensen, O. M.; and van Breugel, K., "Autogenous Shrinkage in High-Performance Cement Paste: An Evaluation of Basic Mechanisms," *Cement and Concrete Research*, V. 33, No. 2, 2003, pp. 223-232.

6. Bentz, D. P.; Garboczi, E. J.; Jennings, H. M.; and Quenard, D. A., "Multi-Scale Digital-Image-Based Modelling of Cement-Based Materials," *Materials Research Society Symposium—Proceedings*, Microstructure of Cement-Based Systems/Bonding and Interfaces in Cementitious Materials, V. 370, 1995, pp. 33-41.

7. Neubauer, C. M.; Jennings, H. M.; and Garboczi, E. J., "Three-Phase Model of the Elastic and Shrinkage Properties of Mortar," *Advanced Cement Based Materials*, V. 4, No. 1, 1996, pp. 6-20.

8. Hua, C.; Ehrlacher, A.; and Acker, P., "Analyses and Models of the Autogenous Shrinkage of Hardening Cement Paste II. Modelling at Scale of Hydrating Grains," *Cement and Concrete Research*, V. 27, No. 2, 1997, pp. 245-258.

9. Xi, Y., and Jennings, H. M., "Shrinkage of Cement Paste and Concrete Modeled by a Multiscale Effective Homogeneous Theory," *Materials and Structures*, V. 30, 1997, pp. 329-339.

10. Mabrouk, R.; Ishida, T.; and Maekawa, K., "A Unified Solidification Model of Hardening Concrete Composite for Predicting the Young Age Behavior of Concrete," *Cement and Concrete Composites*, V. 26, No. 5, 2004, pp. 453-461.

11. Eguchi, K., and Teranishi, K., "Prediction Equation of Drying Shrinkage of Concrete Based on Composite Model," *Cement and Concrete Research*, V. 35, No. 3, 2005, pp. 483-493.

12. Haecker, C. J.; Garboczi, G. J.; Bullard, J. W.; Bohn, R. B.; Sun, Z.; Shah, S. P.; and Voigt, T., "Modeling the Linear Elastic Properties of Portland Cement Paste," *Cement and Concrete Research*, V. 35, No. 10, 2005, pp. 1948-1960.

13. Bažant, Z. P., and Prasannan, S., "Solidification Theory for Concrete Creep I: Formulation," *Journal of Engineering Mechanics*, V. 115, No. 8, 1989, pp. 1691-1703.

14. Ulm, F.-J.; Constantinides, G.; and Heukamp, F. H., "Is Concrete a Poromechanics Material? A Multiscale Investigation of Poroelastic Properties,"

Materials and Structures, V. 37, No. 265, 2004, pp. 43-58.

15. Lin, F., "Modeling of Hydration Kinetics and Shrinkage of Portland Cement Paste," PhD thesis, Columbia University, New York, 2006, 139 pp.

16. Coussy, O., *Poromechanics*, John Wiley & Sons, New York, 2004, 298 pp.

17. Bernard, O.; Ulm, F.-J.; and Lemarchand, E., "A Multiscale Micromechanics-Hydration Model for the Early-Age Elastic Properties of Cement-Based Materials," *Cement and Concrete Research*, V. 33, No. 9, 2003, pp. 1293-1309.

18. Nielsen, L. F., "Beton og Lignende Materialers Stivhed: En Ny Rationel Prediktionsmetoide," *Technical Report* No. 208, Institute of Building Materials, Technical University of Denmark, 1990, 27 pp. (in Danish)

19. Nielsen, L. F., "Porøse Materialers Stivhed," *Technical Report* No. 287, Institute of Building Materials, Technical University of Denmark, 1993, 12 pp. (in Danish)

20. Boumiz, A.; Sorrentino, D.; Vernet, C.; and Tenoudji, F. C., "Modelling the Development of the Elastic Moduli as a Function of the Degree of Hydration of Cement Pastes and Mortars," *Proceedings 13 of the 2nd RILEM Workshop on Hydration and Setting: Why Does Cement Set? An Interdisciplinary Approach*, A. Nonat, ed., Dijon, France, 1997, pp. 295-316.

21. Acker, P., "Micromechanical Analysis of Creep and Shrinkage Mechanisms," *Creep, Shrinkage and Durability Mechanics of Concrete and Other Quasi-Brittle Materials*, F.-J. Ulm, Z. P. Bažant, and F. H. Wittmann, eds., Elsevier Science Publishers B.V., Amsterdam, 2001, pp. 15-25.

22. Velez, K.; Maximilien, S.; Damidot, D.; Fantozzi, G.; and Sorrentino, F., "Determination by Nanoindentation of Elastic Modulus and Hardness of Pure Constituents of Portland Cement Clinker," *Cement and Concrete Research*, V. 31, No. 4, 2001, pp. 555-561.

23. Helmuth, R. A., and Turk, D. H., "Elastic Moduli of Hardened Portland Cement and Tricalcium Silicate Pastes: Effect of Porosity," Symposium on Structure of Portland Cement Paste and Concrete, *Special Report* 90, Highway Research Board, Washington, DC, 1966, pp. 135-144.

24. Tennis, P. D., and Jennings, H. M., "A Model for Two Types of Calcium Silicate Hydrate in the Microstructure of Portland Cement Pastes," *Cement and Concrete Research*, V. 30, No. 6, 2000, pp. 855-863.

25. Constantinides, G., and Ulm, F.-J., "The Effect of Two Types of C-S-H on the Elasticity of Cement-Based Materials: Results from Nanoindentation and Micromechanical Modeling," *Cement and Concrete Research*, V. 34, No. 1, 2004, pp. 67-80.

26. Lide, D. R., *CRC Handbook of Chemistry and Physics*, seventy-eighth edition, CRC Press, Boca Raton, FL, 1997, pp. 6-127.

27. Monteiro, P. J. M., and Chang, C. T., "The Elastic Moduli of Calcium Hydroxide," *Cement and Concrete Research*, V. 25, No. 8, 1995, pp. 1605-1609.

28. Taylor, H. F. W., *Cement Chemistry*, second edition, Thomas Telford Ltd., London, 1997, 459 pp.

29. Mori, T., and Tanaka, K., "Average Stress in Matrix and Average Elastic Energy of Materials with Misfitting Inclusions," *Acta Metallurgica*, V. 21, No. 5, 1973, pp. 571-574.

30. Aboudi, J., *Mechanics of Composite Materials—A Unified Micromechanical Approach*, Elsevier Science Publishers B.V., Amsterdam, 1991, 328 pp.

31. Mindess, S.; Young, J. F.; and Darwin, D., *Concrete*, second edition, Pearson Education, Inc., Upper Saddle River, NJ, 2002, 644 pp.

32. Powers, T. C., and Brownyard, T. L., "Studies of the Physical Properties of Hardened Portland Cement Paste," ACI JOURNAL, *Proceedings* V. 43, 1947, pp. 101-132, 249-336, 469-505, 549-602, 669-712, 845-880, 933-992.

33. Christensen, R. M., *Mechanics of Composite Materials*, John Wiley & Sons, New York, 1979, 348 pp.

34. Christensen, R. M., "A Critical Evaluation for a Class of Micro-Mechanics Models," *Journal of Mechanics and Physics of Solids*, V. 38, No. 3, 1990, pp. 379-404.

35. Bentz, D. P., and Garboczi, E. J., "Percolation of Phases in a Three-Dimensional Cement Paste Microstructural Model," *Cement and Concrete Research*, V. 21, No. 2-3, 1991, pp. 325-344.

36. Bentz, D. P., "Three-Dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development," *Journal of American Ceramic Society*, V. 80, No. 1, 1997, pp. 3-21.

37. Brunauer, S.; Yudenfreund, M.; Odler, I.; and Skalny, J., "Hardened Portland Cement Pastes of Low Porosity VI: Mechanism of the Hydration Process," *Cement and Concrete Research*, V. 3, 1973, pp. 129-147.

38. Herve, E., and Zaoui, A., "Modeling the Effective Behavior of Nonlinear Matrix-Inclusion Composites," *European Journal of Mechanics*, A/Solids, V. 9, No. 6, 1990, pp. 505-515.

39. Perzyna, P., "Fundamental Problems in Viscoplasticity," *Advances in Applied Mechanics*, V. 9, 1966, pp. 243-377.

40. Horita, T., and Nawa, T., "The Effect of Water to Cement Ratio on the Autogenous Shrinkage of Cement Paste," *Journal of Structural and Construction Engineering*, AIJ, No. 565, 2003, pp. 1-7. (in Japanese)

41. Baroghel-Bouny, V.; Mounanga, P.; Loukili, A.; and Khelidj, A., "From Chemical and Microstructural Evolution of Cement Pastes to the Development of Autogenous Deformations," *Autogenous Deformation of Concrete*, SP-220, O. M. Jensen, D. P. Bentz, and P. Lura, eds., American Concrete Institute, Farmington Hills, MI, 2004, pp. 1-21.

42. Koenders, E. A. B., "Simulation of Volume Changes in Hardening Cement-Based Materials," PhD thesis, Delft University of Technology, Delft, the Netherlands, 1997, 171 pp.