

The role of dissolution on irreversible deformation of cement paste

Xiaodan Li¹ and Zachary C. Grasley²

Abstract

A portion of the time-dependent deformation of cementitious materials is irreversible and path dependent. Relevant time-dependent deformations with irreversible components include desiccation shrinkage, carbonation shrinkage, thermal dilation, and creep. Historically, investigations into the mechanisms of the aforementioned deformations have focused on the role of the calcium silicate hydrate (C-S-H) phase; while C-S-H response is important, it is not sufficient to explain irreversible deformation of cement pastes. Here, we discuss the significant contribution that dissolution of cement grains make to irreversible deformation, with the magnitude of contribution quantified via a unique, computationally-implemented modeling approach.

1. Xiaodan Li is a Ph.D. candidate at Texas A&M University, College Station, TX 77840 (email: xiaodanl@tamu.edu).
2. Zachary C. Grasley is an associate professor at Texas A&M University, College Station, TX 77840 (email: zgrasley@tamu.edu).

I. INTRODUCTION

Cement paste exhibits time-dependent deformation in addition to the instantaneous elastic effects under internal/external stimuli (mechanical loading, movement of pore solution, etc.), and a portion of this deformation is path dependent and irreversible. Mechanisms behind this deformation have been investigated by many researchers, and the calcium silicate hydrate (C-S-H) phase has been historically believed to play a dominant role in the time-dependent behavior of cement paste. In reality, irreversible, time-dependent deformation of cement paste is a multi-mechanism process that is exceedingly complex. Indeed, uncovering and accurately modeling the time-dependent deformation process is a *Grand Challenge* facing mechanicians and materials scientists studying cementitious materials.

Recently, a computational scheme coupling a microstructure evolution model and a time-stepping finite element analysis routine has been developed to predict the time dependent deformation behavior of cementitious materials [1, 2]. The simulation results suggest that dissolution of solid load bearing constituents leads to significant time-dependent deformation. As the cement grain dissolution process during the hydration reaction is irreversible, it is hypothesized that a portion of the irreversible deformation of cement paste is associated with the dissolution-precipitation of load bearing cement grains.

The objective of this paper is to simulate the time-dependent behavior of cement paste due to combined elastic deformation of the composite microstructure and the concurrent dissolution of cement grains under the condition of external mechanical loading and desiccation loading. Both the external mechanical loading and desiccation loading result in establishment of a stress field in the cement paste composite, leading to reversible and irreversible deformation. The analysis of the irreversible component of the time-dependent deformation is the focus of this work.

II. COMPUTATIONALLY IMPLEMENTED MODEL

A. Microstructure Model

The hydration model THAMES (Thermodynamic Hydration And Microstructure Evolution) [3, 4] was used to simulate the microstructure evolution at the micrometer level during the hydration process. With the input of the original measured clinker constituent mass fractions, the particle size distribution of the cement and the water to cement mass ratio (w/c) at the sub-particle level, THAMES simulates the dissolution process of cement grains at different time steps (which represent different ages). According to empirically derived equations for clinker reaction rates [5], and based in part on phenomenological dissolution kinetics [3], THAMES

calculates the pore fluid elemental composition at each time step. A thermodynamic engine GEMS (Gibbs Energy Minimization) [6, 7] was implemented in THAMES to calculate the equilibrium solution speciation and the mass of each solid constituent in equilibrium with the solution at each time step. More detailed description of the microstructure model THAMES can be found in [1-3].

B. Finite Analysis

To predict the time-dependent, apparent viscoelastic/viscoplastic (VE/VP) behavior of cementitious composites, the computational scheme was discretized in time to account for the time and (stress or strain) history dependent mechanical properties. Here, the term ‘‘apparent VE/VP’’ is reserved for modeling the constitutive behavior at the macroscale induced by smaller length scale mechanisms that are not due to inherent VE or VP behavior of phases (e.g., C-S-H) within the composite material, but purely due to dissolution of load bearing phases. At each time step in the finite element calculations, THAMES provides 3D snapshots for cement paste as time evolves, where the 3D snapshots of microstructures are meshed into voxels using a spatially aligned numerical discretization [8] such that each voxel becomes an eight node tri-linear cubic finite element consisting of a unique phase with assigned elastic mechanical properties (e.g., Young’s modulus and Poisson’s ratio) from the literature. These 3D time-evolving microstructures generated by THAMES are subjected to strain-controlled periodic boundary conditions in the finite element analyses, and through minimizing the total mechanical energy stored in the microstructure at each time step [1], the volume averaged stress of the composite can be calculated. The composite elastic moduli are calculated by solving the elastic equations on a regular finite element mesh [9], based on the volume averaged stress of the composite.

A key assumption in the model for dissolution of load bearing phases is that once dissolution occurs inside one voxel, the stress originally transmitted by the dissolved solid phases are transmitted into surrounding phases in order to satisfy conservation of linear momentum. Furthermore, the newly formed phases must form in a stress-free state within the deformed configuration that conforms to the preexisting phases. This condition implies that that stress redistribution takes place much faster than chemical phase changes, and the newly formed phases carry no memory of historical responses, resulting in the production of apparent strain inside the microstructure. The term ‘‘apparent strain’’ in this paper is defined, from a continuum mechanics perspective, as strain that exists independent of the state of stress. Unlike other ‘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. This process of microstructure evolution (or load bearing solids dissolution) would lead to apparent VE/VP effects of cement paste even when each microscopic phase is strictly elastic. More detailed procedures, theoretical derivations, and the finite element formulation of the computational model may be found in [1, 2].

C. Stress Controlled Boundary Condition and Shrinkage Prediction

Due to the limitation of the computational scheme that the microstructures in the model can only be subjected to strain-controlled periodic boundary conditions, to predict the time-evolving strain of the macroscopic cement paste composite under constant external stress (stress control) or zero external stress combined with negative internal pore fluid pressure (shrinkage), Boltzmann's superposition principle [10, 11] was applied.

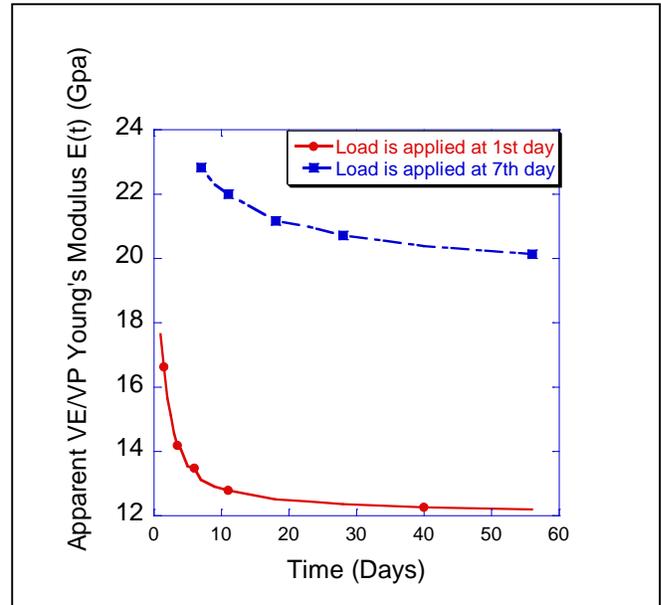
In the computational program, starting with one microstructure at a certain loading age, prescribed, periodic volumetric strain was applied on the boundaries of a series of isotropic, evolving microstructures to determine the evolution of the apparent VE/VP bulk modulus of the whole composite under a specific loading age. In this way, the apparent VE/VP bulk modulus of the cement paste composite under a series of different loading ages can be predicted by the computational scheme. For the mechanical loading case, with the known apparent VE/VP bulk modulus at different ages and the time-evolving apparent volumetric stress, the strain that must necessarily be applied at each time step to maintain an overall spatially averaged constant stress state can be calculated according to the superposition principle. Similarly, to predict time-evolution of the shrinkage strain, the applied periodic boundary volumetric strain was assigned to be zero for all time steps while assigning a negative pore pressure to the fluid phases, the evolution of volumetric stress of the whole composite can be calculated in the computational implemented model. Then, the strain that must necessarily be applied to maintain "free shrinkage" (zero averaged stress) can be calculated. In this way, the predicted time-evolution of the shrinkage strain is due to concomitant elastic deformation of the solid microstructure with changes in pore fluid pressure and dissolution of cement grains and subsequent stress redistributions in the microstructure.

III. SIMULATION RESULTS AND DISCUSSIONS

A. External Mechanical Loading

Microstructures of hydrating cement composites with pure elastic phases (using elastic properties taken from [12]) at different ages (from 1 d to 56 d) were examined in this project. In these simulations, the irreversible, time-dependent shrinkage of the cement pastes occurs strictly due to the time-dependent dissolution of cement grains. Fig. 1 shows the

Fig. 1. 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.



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. From the predicted results, one can see that the apparent VE/VP behavior caused by dissolution of cement grains is substantial in cement paste composites. The decreasing rate of relaxation of cement paste with age (because the hydration rate slows as cement paste ages) successfully demonstrates the well-known aging effect of cement paste.

When predicting the linear strain of 0.40 w/c cement paste when the cement paste is subjected to controlled stress boundary condition at 273 K, Fig. 2 is obtained. In this figure, constant loadings initiated at the age of 1 d and 4 d were applied on cement paste for a loading duration of 5 d, as shown on the right hand Y axis in Fig. 2. The solid lines show the overall predicted linear strain due to combined cement grain dissolution effects and elastic deformation. In both figures, cement paste experiences instantaneous elastic deformation at the time of application and removal of the external loading. After the loadings are completely removed, cement paste would not recover back to its initial configuration, but to a deformed configuration with permanent irreversible strains. These residual strains exist partially because at the time of the removal of the load, the elastic deformation of cement paste would not be as large as when the load is first applied (as a result of the increasing

stiffness with time). Another major reason for the residual, irreversible strains is that cement grain dissolution during the hydration reaction leads to significant irreversible creep (Fig. 2) due to the fact that phases that precipitate after the load has been applied are in a state of zero stress even while the composite is under load. When loaded at an earlier age, a much larger irreversible strain would be observed due to the more active hydration reaction at earlier ages (and thus higher dissolution rate of cement grains).

B. Desiccation Shrinkage

Fig. 3 shows the predicted irreversible shrinkage strain normalized by the applied pore fluid pressure for a 0.40 w/c

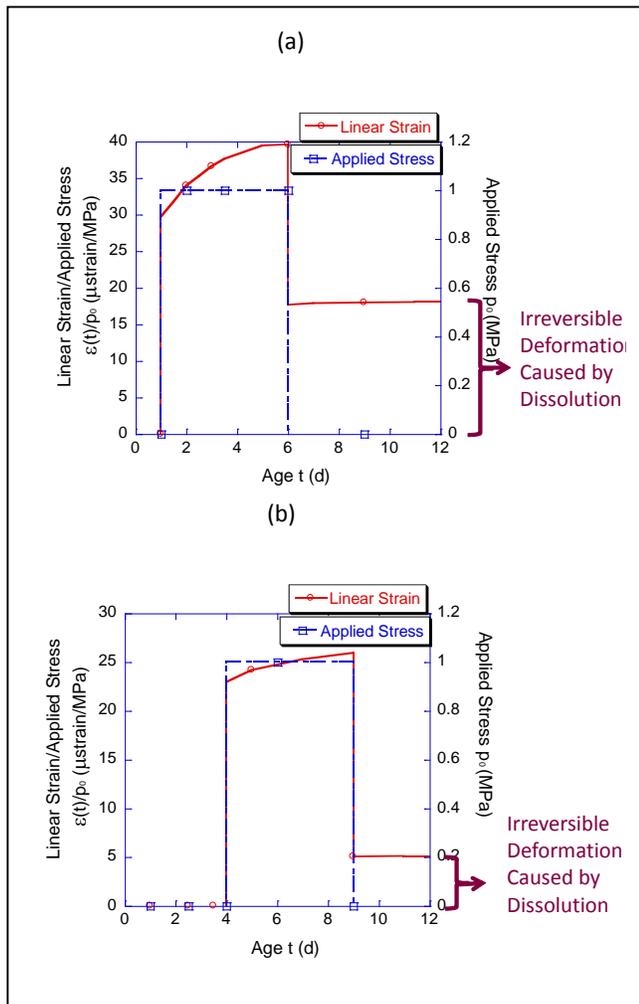


Fig. 2. Predicted linear (axial) strain of 0.40 w/c cement paste when loaded uniaxially at ages of (a) 1 d and (b) 4 d. In both graphs, the load is applied for a period of 5 d with the loading history shown in the graph on the right hand Y axis. The solid lines show the overall strain due to the cement grain dissolution effects and instantaneous elastic deformation.

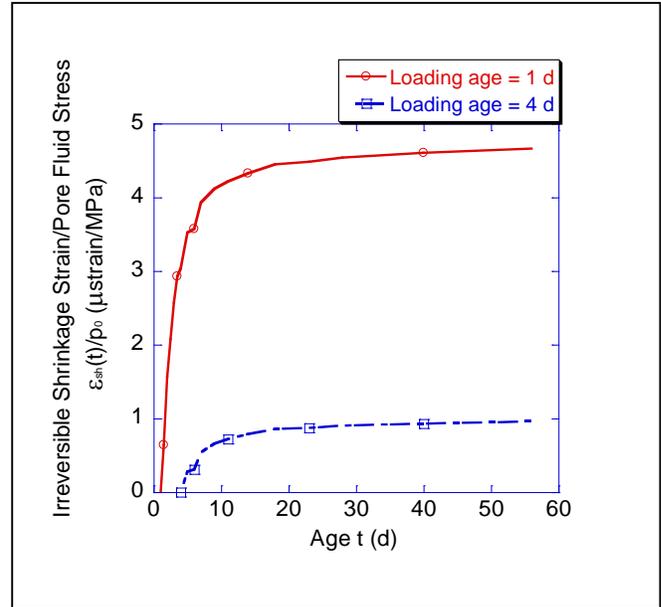


Fig. 3. Irreversible shrinkage strain normalized by the applied pore fluid pressure in a 0.40 w/c cement paste when dried at different ages (1 d and 4 d). In this graph, irreversible shrinkage strain was considered to increase strictly due to dissolution of load bearing cement grains.

Another reason leading to the faster shrinkage for the younger specimen is that more water is present in younger specimens, and thus the negative pressure results in greater contraction of the solid skeleton. Meanwhile, the younger cement paste composite is less stiff than the older cement paste, and thus is more compliant to external and internal forces, resulting in a much larger deformation. Both specimens show decreasing irreversible shrinkage rate with age because hydration rate decreases as cement paste ages. Thus, in conclusion, from the simulation results, younger cement pastes are likely to exhibit greater irreversible shrinkage from cement grain dissolution than older cement pastes.

In actual, drying porous bodies, the pore fluid pressure approximately changes with age as a function of the time-evolving internal relative humidity (RH) through the combined Kelvin-Laplace equation

$$\{1\} p \approx -\ln\left(\frac{RH}{RH_0}\right) \frac{RT}{v_w},$$

where p is the pore fluid pore pressure, RH is the current internal relative humidity, RH₀ is the reference configuration internal relative humidity, R is the universal gas constant, v_w is the molar volume of water, and T is the temperature in Kelvins [13]. Here, the time-evolution of the effect of the dissolved species on the chemical potential of the pore fluid is neglected; a modified version of eq. {1} should be used if one wishes to simulate evolving chemistry of the pore solution during desiccation [14]. With the experimental data of the time-evolving RH, the pore fluid pressure inside the

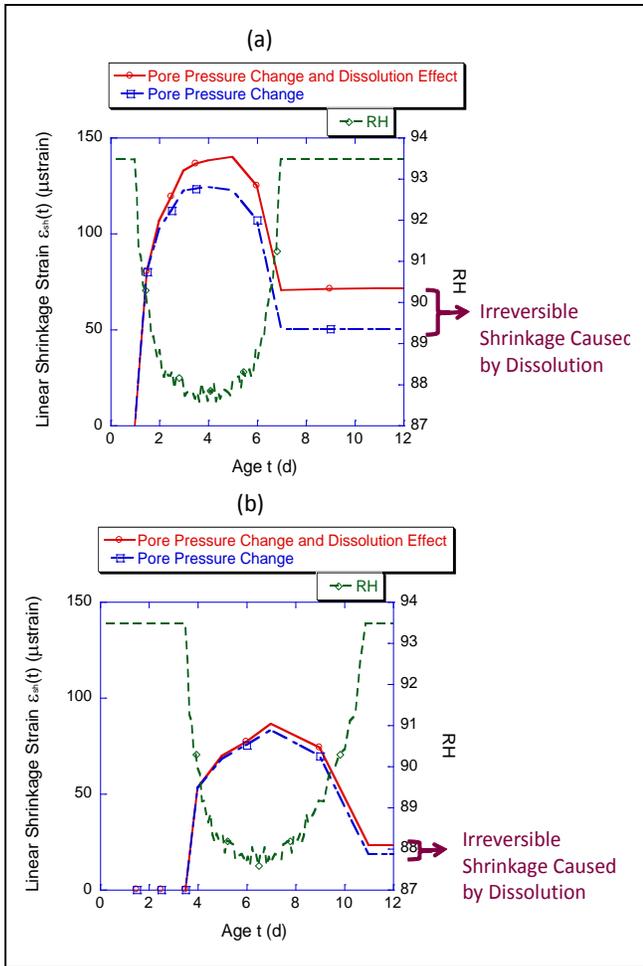


Fig. 4. Predicted shrinkage strain of 0.40 w/c cement paste with drying (and subsequent re-wetting) initiated at ages of (a) 1 d and (b) 3.5 d. In both graphs, the solid lines show the overall shrinkage due to both pore pressure change and cement grain dissolution effects, while the dashed shrinkage lines show the recoverable shrinkage of cement paste occurring purely due to pore pressure change. Internal RH history was also included in this graph on the right hand Y axis.

cement paste composite can be calculated and implemented into the computational scheme to simulate realistic shrinkage behavior of cement paste.

At different ages of drying initiation of 1 d and 3.5 d, when using the experimental data of time-evolving RH while forcing RH to return back to its initial value (to simulate re-wetting) after several days of drying, the results shown in Fig. 4 can be obtained. Microstructures of 0.40 w/c cement paste were used in the simulations, and the temperature was kept constant at 273 K. The solid shrinkage lines show the overall shrinkage due to both pore pressure change and cement grain dissolution effects, and the dashed shrinkage lines show the predicted shrinkage of cement paste occurring purely due to pore pressure change. In both figures, cement paste shrinks

with decreasing RH and swells with recovering RH. After RH returns back to its initial value, the irreversible shrinkage strains caused by dissolution may be predicted by the differences between the solid lines and the dashed lines. In comparison to Fig. 4 (b), Fig. 4 (a) shows the predicted shrinkage strain history of cement paste when drying initialized at an earlier age, and similarly to the case under external loading, it can be seen that when dried at earlier ages, a much larger irreversible shrinkage would be observed due to the more active hydration reaction at earlier ages. These results suggest that steps to increase the degree of hydration prior to drying initiation (e.g., wet curing and heat curing) would reduce the irreversible component of desiccation shrinkage.

IV. CONCLUSION

A computational scheme that couples a microstructure evolution model and a time-stepping finite element method capable of tracking phase formation/dissolution was utilized to predict the irreversible strain of cement paste. From the model simulations, dissolution of cement grains of hydrating cement paste is a significant factor leading to the irreversible component of cement paste deformation for both cases of mechanical loading and desiccation loading. The simulations also imply that irreversible deformation is closely related to age; delayed loading and drying would lead to drastic reductions in irreversible deformation associated with cement grain dissolution.

REFERENCES

- [1] X. Li, Z. C. Grasley, E. J. Garboczi, and J. W. Bullard, "Modeling the apparent and intrinsic viscoelastic relaxation of hydrating cement paste," *Cement and Concrete Composite*, vol. 55, pp. 322-330, 2015.
- [2] X. Li, Z. C. Grasley, E. J. Garboczi, and J. W. Bullard, "Computing the time evolution of the apparent viscoelastic/viscoplastic Poisson's ratio of hydrating cement paste," *Cement and Concrete Composite*, vol. 56, pp. 121-133, 2015.
- [3] J. W. Bullard, B. Lothenbach, P. E. Stutzman, and K. A. Snyder, "Coupling thermodynamics and digital image models to simulate hydration and microstructure development of portland cement pastes," *Journal of Materials Research*, vol. 26, pp. 609-622, 2011.
- [4] B. Lothenbach and F. Winnefeld, "Thermodynamic modelling of the hydration of portland cement," *Cement and Concrete Research*, vol. 36, pp. 209-226, 2006.
- [5] L. Parrot and D. Killoh, "Prediction of cement hydration," in *Proc. Br. Ceram. Soc.*, 1984, p. 41.
- [6] D. A. Kulik, "Gibbs energy minimization approach to modeling sorption equilibria at the mineral-water interface: Thermodynamic relations for multi-site-surface complexation," *American Journal of Science*, vol. 302, pp. 227-279, March 2002 2002.
- [7] D. A. Kulik, "Dual-thermodynamic estimation of stoichiometry and stability of solid solution end members in aqueous–solid solution systems," *Chemical Geology*, vol. 225, pp. 189-212, 2006.
- [8] W. Ruetz, *A hypothesis for the creep of hardened cement paste and the influence of simultaneous shrinkage Proceedings of International Conference On the Structure of Concrete*. London, England: Cement and Concrete Association, 1968.
- [9] T. I. Zohdi, "Homogenization Methods and Multiscale Modeling," in *Encyclopedia of Computational Mechanics*, ed: John Wiley & Sons, Ltd, 2004.
- [10] A. S. Wineman and K. R. Rajagopal, *Mechanical response of polymers: an introduction*: Cambridge University Press, 2000.
- [11] R. Christensen, *Theory of viscoelasticity: an introduction*: Elsevier, 2012.
- [12] C. J. Haecker, E. J. Garboczi, J. W. Bullard, R. B. Bohn, Z. Sun, S. P. Shah, *et al.*, "Modeling the linear elastic properties of Portland cement paste," *Cement and Concrete Research*, vol. 35, pp. 1948-1960, 2005.
- [13] R. Defay, A. Bellemans, and I. Prigogine, *Surface tension and adsorption*: Longmans London, 1966.
- [14] Z. Grasley and K. Rajagopal, "Revisiting total, matric, and osmotic suction in partially saturated geomaterials," *Zeitschrift für angewandte Mathematik und Physik*, vol. 63, pp. 373-394, 2012/04/01 2012.