Microstructural origins of cement paste degradation by external sulfate attack

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HIGHLIGHTS

- A new microstructure model simulates reaction-induced expansion in sulfate attack.
- Constrained AFt grows at the expense of a series of less stable Al-phases.
- Localized deformation and the onset of damage are predicted.
- Spatial distribution of monosulfate influences the severity of damage.
- The model predicts mitigation of damage by adding Mg or carbonates.

ARTICLE INFO

ABSTRACT

A microstructure model has been applied to simulate near-surface degradation of portland cement paste in contact with a sodium sulfate solution. This new model uses thermodynamic equilibrium calculations to guide both compositional and microstructure changes. It predicts localized deformation and the onset of damage by coupling the confined growth of new solids with linear thermoelastic finite element calculations of stress and strain fields. Constrained ettringite growth happens primarily at the expense of calcium monosulfoaluminate, carboaluminate and aluminum-rich hydrotalcite, if any, respectively. Expansion and damage can be mitigated chemically by increasing carbonate and magnesium concentrations or microstructurally by inducing a finer dispersion of monosulfate.

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1. Introduction

The degradation of cementitious materials by external sulfate attack is one of the most frequently cited causes of service life reduction of concrete structures. The importance of sulfate attack is attested by the multitude of experimental and theoretical studies on its origin and manifestations that have been published just in the last decade [1–22]. Such investigations have consistently indicated that sulfate attack is a complicated, multiscale and multiphysics process involving the coupling of physical, chemical, and mechanical interactions.

The formation of ettringite [23–25] and sometimes gypsum [26] are usually thought to be responsible for significant volumetric expansion and structural damage during sulfate attack. Several of the proposed mechanisms of ettringite-related expansion (e.g., solid state conversion [27,28], volume increase [29], colloidal swelling [30]) often do not match experimental observations and measurements [21,15]. More recently, crystallization pressure theory has shown that stress exerted on pore walls by impingement of growing crystals is significant only in confined spaces and when the surrounding solution is highly supersaturated with respect to those crystals [31–33]. Accordingly, macroscopic stress during sulfate attack is determined more by the locations of active ettringite growth in the microstructure rather than the total volume of ettringite formed [21,18]. That is, the origin and extent of sulfate-induced expansion is the transformation to ettringite of AFm phases that are dispersed within the fine porosity of C–S–H gel [15].

Various approaches have been used to simulate the effects of sulfate attack. A multiionic transport model [34] has been used to simulate the evolution of mineral phases in cement-based

materials exposed to aggressive environments such as sulfate solution [35,36]. Infilling of capillary porosity by precipitated solids and the resulting displacement of liquid from the material has been simulated by a finite-difference approach for nonsteady-state diffusion and reaction of ions in cementitious composites [37,10]. Other reaction–diffusion models have been applied to the corrosion of building materials subjected to sulfate attack [38], although models of this kind require knowledge of the transport properties and porosity within the material. Expansion and damage have been simulated using continuum damage mechanics at the millimeter length scale [4,5,9,16,17]. In particular, the finite element model developed by Idiart [17] simulates the millimeter-scale distribution of ettringite and development of expansion cracks around aggregates embedded within an homogenized cementitious binder.

Modeling of sulfate attack at the scale of the cementitious binder microstructure has not been reported, but nevertheless could be valuable for deepening our understanding of the origin and mechanisms of sulfate-induced degradation. In this paper, we report a first step in this direction. A thermodynamic-microstructural model of hydration [39] is coupled to a linear thermoelastic finite element model [40] to simulate microstructural evolution by external sulfate attack and to track the microscopic stress field that develops by constrained ettringite growth in the binder porosity. The model is applied here to simulate near-surface sulfate attack of Type I ordinary portland cement binder in a sodium sulfate solution. We also investigate the sensitivity of the model predictions to the spatial distribution of aluminate-bearing phases in the microstructure. Finally, the model is used to simulate and compare the differences in the progress of sulfate attack among three types of cement having different aluminate contents.

2. Model description and technique

2.1. Simulating hydration

The model used here is an extension of the Thermodynamic Hydration and Microstructure Evolution (THAMES) model recently developed at the National Institute of Standards and Technology (NIST) [39]. THAMES has three main components: (1) a kinetic model of cement clinker phase dissolution, which determines the time dependence of elemental concentrations in the pore solution [41]; (2) thermodynamic speciation calculations to determine the equilibrium composition and abundance of phases other than clinker minerals, including the pore solution [42–44]; and (3) a 3D digital image model for spatially distributing these various phases to represent the microstructure of the binder. Full details about how these three components work together is provided elsewhere [39,45]. Briefly, each a 1 μm^3 of space is represented by a voxel in the microstructure having an integer identifier unique to the phase occupying that volume. Each voxel sharing one or more faces with a different phase is identified as an "interface" voxel and stored in lists of sites eligible for dissolution or growth of that phase. The list members are evaluated for their potential to dissolve or grow, respectively, by assigning an "affinity" at each interface voxel that characterizes the relative tendency of a given phase to grow in the environment at that site. A negative affinity between two phases means that increases in the interface between them is unfavorable, while a positive affinity between two phases tends to promote the increase of that interface. This concept of affinity does not have any well-defined thermodynamic significance in terms of crystal growth theory, but is used merely as a convenience to generate different growth morphologies. In the future, it may be possible to establish a stronger link between the affinities and physical parameters such as interfacial energy and growth mobility of interfaces as a function of orientation. Consistent with the observations of

Schmidt and coworkers [15], we assume that the transformation to ettringite of aluminate-bearing phases that are finely dispersed within C–S–H give rise to stress fields that are responsible for expansion. Therefore, we adopt affinity values that promote the fine intergrowth with C–S–H of calcium monosulfoaluminate (hereafter called monosulfate), calcium mono- and hemicarboaluminate (hereafter called monocarbonate and hemicarbonate, respectively), and hydrotalcite.

2.2. Simulating interaction with Na_2SO_4

Hydration was stopped at 100 days of hydration and the simulation of sulfate attack was started. 100 days of hydration was chosen arbitrarily, but we note that the degree of hydration at this time is 0.90, based on mass of clinker consumed, so further hydration happens quite slowly. Therefore, ignoring further hydration from that point is likely a good approximation. The simulation begins by flushing the capillary pore volume with a 0.1 mol kg^{-1} Na_2SO_4 solution, using an algorithm reported recently [45]. The total mass of water in the aqueous solution phase is first retrieved from the current equilibrium state, together with the molal concentrations of the primary solute species $[SO_4^{2-}]$ and $[Na^+]$. From these data, calculations are made of the number of moles of each of these ions that must be added to, or removed from, the solution to increase or decrease, respectively, their molal concentration to prescribed initial values prior to each cycle's equilibration step. $[K^+]$ and $[Ca^{2+}]$ were also set in the same manner to 0.5 mmol kg^{-1} and 0.1 μmol kg^{-1}, respectively, prior to equilibration, a minimum value chosen to avoid numerical instabilities in the thermodynamic calculations while still enabling the process of calcium leaching which is observed in sulfate attack experiments [46,47].

The thermodynamic system is re-equilibrated with the newly flushed sulfate solution. Phase transformations are assumed to be dictated by thermodynamic equilibrium between the solid phases and solution, altering both the solution speciation and the volumes of different solid phases. The microstructure is updated according to the aforementioned rules, adding or subtracting voxels of each phase corresponding to that phase's net volume fraction change. The model repeats the process of flushing, re-equilibration, and microstructure updates. The physical time associated with each of these flushing cycles would be determined by (1) the time required to exchange the pore solution with fresh solution, and (2) the time required for the fresh solution to reach equilibrium with the remaining solids. Either of these processes could, in principle, control the time scale of a given flushing cycle. In typical experiments on sulfate attack, the specimen is submerged in a sulfate solution of fixed composition, so solute diffusion from the interior capillary pore space probably controls the rate of degradation everywhere except very near the exterior surface, where the rate is likely controlled by mineral dissolution or growth. The present study does not attempt to capture the complexities of diffusion-controlled solute migration to the interior of the specimen. Instead, our purpose is to explore the overall course of early degradation at the specimen surface (i.e., the first 100 μm layer) in terms of microstructure development, expansion, and the onset of damage. With this microstructure modeling capability established, a subsequent study will explore microstructure development and expansion as a function of depth by coupling the thermodynamic-microstructure model to a reaction–diffusion framework similar to that employed by others for modeling at the macroscopic scale [17].

2.3. Elastic strain and stress calculations

Ettringite has a greater molar volume than the aluminate-bearing phases from which it forms, and we assume it