



A model investigation of the mechanisms of external sulfate attack on portland cement binders

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HIGHLIGHTS

- A microstructure model simulates crystallization pressure induced expansion in sulfate attack.
- Damage of microstructures at different depths alters the rates of sulfate ingress.
- Insights of sulfate attack mechanism are given.
- Reduction of pH of the pore solution destabilizes AFm when carbonates are present.
- AFm can spontaneously transform to AFt without any additional sulfate addition.

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ABSTRACT

A recent microstructural model for simulating external sulfate attack on cement paste is used to calculate the driving force for local expansive growth of AFt phase in terms of crystallization pressure, and the strain and stress fields are tracked within the microstructure with micrometer-scale resolution using a linear elastic finite element model. Damage induced by expansion modifies both the local effective transport properties and linear elastic properties of each microstructure at different depths, and thereby potentially alters the rates of sulfate ingress and expansion. Simulations give insight about sulfate attack mechanisms, which are investigated in more detail by separating the individual influences of sulfate concentration and pH of the pore solution. Especially when soluble carbonates are present, reductions in the pore solution pH, which often accompany ingress of sulfates, significantly destabilizes calcium monosulfoaluminate and accelerates AFt growth. In fact, within a narrow pH range some calcium monosulfoaluminate can spontaneously transform to AFt without any additional sulfate addition. Therefore, the progress of phase transformations and expansion from the surface to the interior of the porous material is dictated by the rate of ingress of concentration fronts of both sulfate ions and pH, which do not necessarily coincide.

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1. Introduction

External sulfate attack, the ingress of sulfate ions from the environment into concrete, can lead to expansion and damage caused by the precipitation of AFt¹ [1–3] and sometimes gypsum [4] within

the hardened material. This process of gradual concrete degradation is challenging to understand or predict quantitatively. Part of the reason for this is that the underlying chemical and physical mechanisms are not fully understood. External sulfate attack of concrete involves a complex coupling of chemical processes (e.g., ion diffusion and phase transformations induced by composition changes in the aqueous solution) and mechanical responses (e.g., local deformation, expansion, and cracking). In part because of these couplings, the details of the individual mechanisms have not been settled despite decades of research, although the expansion and material failure due to sulfate ingress is generally agreed to be caused by the conversion of calcium monosulfoaluminate to AFt [5–7]. Localized crystallization pressure [8–10] induced by the precipitation of AFt in small

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¹ Ettringite is one limiting composition of a family of compositions possible for a phase designated as AFt that typically forms during hydration and sulfate attack. Because the AFt composition is usually heavily weighted toward ettringite, the two terms are sometimes used interchangeably.

pores has come to be generally accepted as the driving force for observed expansion and damage of paste and mortar specimens [11,12].

Various approaches have been used to simulate sulfate attack on mortar or concrete at the millimeter length scale, at which aggregate can be resolved explicitly but the binder and capillary porosity are homogenized as a continuum. These approaches employ continuum damage mechanics and coupled reactive transport and mechanical modeling [13–19]. Microstructure modeling, on the other hand, offers the ability to calculate localized driving forces, potential for damage and relate these to evolving material properties. However, models of sulfate attack at the micrometer length scale are rare [20,21]. For example, Feng et al. resolved a detailed, virtual 3D (i.e., three dimensional) microstructure as a digital image with $1\mu\text{m}$ resolution, in which individual phases and their spatial distribution are clearly delineated along with a realistic particle and pore morphology and topology [22]. In that model, phase transformations caused by hydration or by the introduction of a sodium sulfate solution were estimated according to equilibrium thermodynamic assumptions. Expansion was modeled as a local misfit strain when AFt forms in pores that are too small compared to the stress-free volume of the AFt precipitate. And the corresponding heterogeneous stress field was calculated using a linear thermoelastic FE model. In that first detailed microstructure modeling study of sulfate attack, sodium sulfate solution was introduced by total replacement of the existing pore solution within a small microstructure element; ion diffusion within that microstructure was not explicitly modeled [22], so the study was applicable only to the material adjacent to the exterior surface.

In this paper, a recently modified version [23] of the same thermodynamic-microstructural model is used to include a more realistic crystallization pressure driving force for expansion and to simulate the diffusion of mobile species within a macroscopic prismatic cement paste specimen. The results focus on the separate but interrelated ways that sulfate ion concentration, pH, and carbonate ion concentration influence the driving force for phase transformations, and how those phase transformations affect the course of expansion and damage. The simulations indicate that a reduction of pH by itself can cause the rapid and significant transformation of monosulfate to ettringite for both low and high sulfate concentrations simulated in this paper. And this pH effect does not necessarily apply in systems where no carbonate exist.

2. Modeling

The computational volume element is built up from well-hydrated subsystems with dimensions $100\mu \times 100\mu \times 100\mu$. These subsystems are generated from experimental data by a method, described fully by Bullard et al. [24], which will be briefly outlined here. The particle size distribution is measured by laser scattering from a dilute alcohol suspension [25]. The three-dimensional shape distribution of the particles are characterized by X-ray microcomputed tomography and subsequently modeled by spherical harmonic expansion [26]. Phase abundance of the unhydrated cement is characterized by Rietveld refinement of its powder X-ray diffraction pattern [27], and the spatial distribution of the phases is quantified using two-point correlation functions measured on phase segmented microstructure images of cut and polished specimens obtained by scanning electron microscopy and X-ray microanalysis [28]. A three-dimensional virtual microstructure of a real portland cement paste (proficiency sample 168, Cement and Concrete Reference Laboratory, Frederick, MD [29]) with a desired water-to-cement mass ratio (w), is reconstructed from experimental measurements of particle size and shape distributions [25,26]. Quantitative analysis of phases and their spatial distribution in

the unhydrated powder are characterized by quantitative X-ray powder diffraction [27,28]. A 3D digitized paste microstructure is reconstructed from these data by randomly parking particles, starting with the largest and following the measured particle size and shape distribution, within a $100 \times 100 \times 100$ box of cubic voxels; each voxel has a $1\mu\text{m}$ edge length. The phases and their spatial distribution are mapped into the solid particles using methods that have been described extensively elsewhere [26,30–32].

A thermodynamic-microstructure computer model called THAMES [21,22,24] is used to simulate hydration of the simulated paste for 100d at 298K. The model has three interrelated components: (1) an empirical model [33] of the dissolution rate of each of the four major cement clinker phases in portland cement: alite (C_3S),² belite (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF); (2) the GEMS3K thermodynamic equilibrium and speciation model [34–36] for calculating the abundance and composition of condensed phases, including the aqueous solution speciation, which is supplemented with the *cemdata14* thermodynamic database for cementitious phases [37]; and (3) a digital image model for updating and spatially distributing the condensed phases to represent the evolution of the 3D binder microstructure.

Hydration is simulated in discrete time steps. In a given time step, the kinetic model is used to determine the moles of each clinker mineral that should dissolve. The dissolved moles of each independent component (e.g., element or electron) determine the chemical composition of the closed thermodynamic system consisting of the aqueous solution and all hydration products, and the GEMS3K model [34–36] calculates the amount of each phase that minimizes the Gibbs energy for that composition. With the updated molar quantities of each phase, the microstructure model distributes the phases, voxel by voxel, on a volume basis to update the microstructure.

2.1. Sulfate attack simulation

Sulfate attack is assumed to begin after 100d of simulated hydration of a paste with w/c of 0.45 and hydration degree 0.9 [21]. The degradation rate may depend on the degree of hydration at which sulfate attack begins. In laboratories, researchers usually start the sulfate attack experiment after cement pastes are well hydrated. Hydration time before sulfate attack experiment varies from 13 days to 90 days [11,38,39]. In this study, 100d is chosen for no other reason than to ensure that the cement is well hydrated.

At 100d of hydration, the degree of hydration of this binder exceeds 0.9 [22] and further hydration should occur quite slowly; for simplicity the model assumes that hydration stops once sulfate attack begins.

The sample being simulated is a $5\text{ mm} \times 5\text{ mm} \times 5\text{ mm}$ cube, comprising $50 \times 50 \times 50$ “subsystem” elements, with each subsystem being a 3D hydrated microstructure described above. Sulfate attack is simulated at the microstructure scale independently within each subsystem, as described below, depending on the local solution composition. But each subsystem is also upscaled to the macroscopic specimen scale either as a single node of a finite difference mesh (for diffusive transport simulations) or as a single trilinear elastic element in a finite element mesh (for calculations of stress distribution, expansion, and composite elastic moduli) [40]. Therefore each node, or element, has average relative diffusivity and elastic moduli that are calculated directly on the microstructure associated with that node as the microstructure evolves in time. That is, the time and position dependent properties of the material

² Cement chemistry notation is used throughout, according to which C = CaO, S = SiO_2 , A = Al_2O_3 , and F = Fe_2O_3 .

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