



A model of phase stability, microstructure and properties during leaching of portland cement binders



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ABSTRACT

A new model of 3D cement paste microstructure development is described and used to simulate the influence of leaching on hydrated cement pastes. In contrast to recent leaching models that have used empirical rules for phase dissolution, this model uses continual thermodynamic speciation and phase stability calculations to guide the microstructural changes that happen throughout hydration and subsequent exposure to low-pH solutions. This novel aspect of the model enables it to predict not only the well-known phase instability of calcium hydroxide at the onset of leaching, but also the detailed compositional and volumetric changes of C–S–H gel and other calcium, aluminate, and sulfate phases. Besides tracking the compositional and microstructural changes, we use the evolving microstructure as input to calculate changes in the relative diffusivity and effective Young's modulus of the binder using established finite difference and finite element models. The results are broadly consistent with previous experimental and modeling investigations of leaching. In particular, the leaching process can be roughly divided into initial, intermediate, and final stages, each of which has distinct degradation characteristics and consequences for mechanical and transport properties. The thermodynamic basis of the model makes it readily extensible to simulate a wide range of cementitious materials and degradation phenomena, so we discuss its potential as a virtual microprobe for use with continuum-scale service life models of concrete elements.

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1. Introduction

Replacement or rehabilitation of existing concrete structures costs about \$18 billion to \$21 billion each year in the U.S. alone [1]. Chemical deterioration of the cementitious binder is a primary reason for these high costs and represents a major challenge to increased sustainability of the civil infrastructure. Among the various kinds of chemical deterioration, leaching is a progressive extraction of calcium from the cementitious binder caused by contact with moisture having pH significantly lower than that of the alkaline pore solution [2]. As calcium leaches from concrete, its reactions with air or dissolved sulfates can cause efflorescence (i.e., the surface formation of calcium carbonate or calcium sulfate). More importantly, the loss of calcium from the system also leads to dissolution of calcium hydroxide and a corresponding increase in porosity and transport properties of surface concrete [3,4], so

it can lead to accelerated degradation by other forms of chemical attack as well.

Investigations of leaching mechanisms by laboratory experiments are usually difficult and time consuming [5,6], so a considerable effort has been spent on modeling the process. Bentz [3] and Marchand [7] both modeled the influence of the dissolution of portlandite (i.e., calcium hydroxide) on pore structure and transport properties. Aspects of these models were incorporated into computational studies of the mechanical and transport properties of leached cement paste and mortar [8–12]. Berner [13] was perhaps the first to suggest the importance of thermodynamic equilibrium between the pore solution and the solid phases in the cement paste for determining the chemical evolution of a leached binder, and this concept has since been used in several models to describe the mass balance of calcium in the liquid and solid phases [14–19]. Those kinds of models have provided considerable insight into the nature of leaching, its influence on capillary pore volume, and the corresponding changes in transport properties. Even so, the size distribution and connectivity of the capillary porosity, not just total pore

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volume, are important in determining transport properties. Furthermore, a detailed knowledge of the assemblage of solid phases in the binder microstructure can enable accurate calculations of composite properties (e.g., elastic moduli, relative diffusivity) using 3D microstructure-based software tools such as the Virtual Cement and Concrete Testing Laboratory (VCCTL) [20,21].

In this paper, we extend a thermodynamically guided microstructure model of cement hydration [22] to simulate leaching of well-hydrated cement. The approach differs from previous models in three ways. First, we use full geochemical thermodynamic equilibrium calculations to assess both the volume fractions and compositions of the various solid binder phases and the speciation of the pore solution. Second, we link these equilibrium calculations to a digital-image model of 3D microstructure to track changes in the binder microstructure as leaching proceeds. And finally, we use the evolving microstructure explicitly to calculate, using finite element and finite difference models, the changes in Young's modulus and the relative diffusivity of the binder, respectively. In the remainder of the paper, we describe the modeling approach and apply it to simulate leaching of a Type I portland cement. Model predictions of chemical evolution, capillary porosity, Young's modulus, and relative diffusivity are presented and compared to results of previous experimental or modeling investigations.

1.1. Prior investigations of leaching

At least 15 previous studies of leaching, both experimental and modeling, have been reported in the past 20 years, using either plain calcium silicate systems [13,14,17] or portland cement systems [3,4,6–9,12,15,16,23,24]. In general, these investigations have observed three main stages of leaching in well-hydrated systems [9,13,17]:

- An *initial* stage, in which dilution of calcium, alkali, and hydroxyl ions in the leachate causes dissolution of portlandite (CH). During this stage, excess solid CH buffers the solution with respect to calcium and hydroxyl ions, thereby minimizing the dissolution of any other solid phases;
- An *intermediate* stage, which commences as soon as all CH has dissolved and can no longer buffer the solution. At this point the solution pH decreases and initiates the progressive decalcification of C–S–H gel [9,13,16,17];
- A *final* stage, in which most of the calcium content of C–S–H has been lost, leaving behind a high-silica amorphous phase [13]. In principal, other low-solubility calcium aluminate phases may become unstable and dissolve in this stage, too. Much of the material's original mass has been leached away by this stage, making it weak and subject to disintegration.

The computational model used in this paper recovers these three stages. In that sense, the current model does not reveal significantly new phenomena or mechanisms of leaching. However, with the model we are now able to analyze the coupling of the chemical evolution and accompanying changes in microstructure and properties that leaching causes. Modeling of leached microstructures and properties has been reported in the past [3,9,8], but lacked a firm basis in chemical thermodynamics to guide the accompanying phase changes, especially with regard to the decalcification of C–S–H and loss of aluminate phases. Part of our purpose in this paper, therefore, is to compare the results of the current model to those earlier results and to establish better ties between the chemical driving forces for leaching and the ensuing microstructure and property development. Moreover, the model, once validated for leaching phenomena, can be readily extended to analyze other types of degradation such as sulfate attack and carbonation.

2. Model description and technique

2.1. Simulation of hydration

The model used here is based on the Thermodynamic Hydration and Microstructure Evolution (THAMES) model recently developed at the National Institute of Standards and Technology (NIST) [22]. 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; (2) thermodynamic equilibrium calculations to determine the composition and abundance of phases other than clinker minerals, including pore solution composition and speciation, corresponding to a minimum in Gibbs free energy; and (3) a digital image model for spatially distributing these various phases to represent the 3D microstructure of the binder. The dissolution rate of each of the four major clinker phases in portland cement (i.e., C_3S , C_2S , C_3A , and C_4AF)¹ is calculated at each time interval using an empirical model proposed by Parrot and Killoh (PK) [25]. The PK model uses equations to describe alternate mechanisms which could control the rate of hydration at any moment, including nucleation, growth of hydration phases, and diffusion of solute species. These rate equations depend on the instantaneous degree of hydration, the powder's specific surface area as measured by the Blaine fineness, the water-to-cement mass ratio (w/c), temperature, and six empirical parameters that are fit from observations on a wide range of portland cement pastes. The rate is calculated by evaluating the rate equation for each available mechanism and selecting the one that yields the minimum rate.

The thermodynamic component of THAMES is based on the GEMIPM2K thermodynamic model [26], supplemented with a thermodynamic database for the major minerals and hydration products found in cementitious materials [27]. This component is identical to that described elsewhere by Lothenbach [27,28]. Briefly, everything except the clinker minerals is treated as a closed thermodynamic system; the clinker minerals are taken to be outside the thermodynamic system, and their extent of dissolution at any time sets the chemical composition of the thermodynamic system itself. Within the thermodynamic system, three types of matter are defined: (1) independent components (IC), which are chemical elements and electrical charge; (2) dependent components (DC), which are compounds or moieties composed of one or more ICs (e.g., $Ca(OH)_2$, SO_4^{2-}); and (3) phases, which are composed of one or more DCs (e.g., gypsum, aqueous solution). The model constrains the moles of each IC to be fixed at any time step, and the equilibrium distribution of the ICs among the possible DCs and phases, including solution speciation and partitioning of end members in solid solutions, is calculated by "dual-thermodynamic" calculations that minimize the Gibbs free energy [29]. At each time step, the change in elemental composition of the pore solution, based on the amount of dissolution calculated in that time step by the PK model, defines the change in moles of each IC. Again, we repeat for clarity that the undissolved portions of the clinker phases are not part of the thermodynamic system.

An important point for this study is that the calcium silicate hydrate (C–S–H) gel is modeled as a nonstoichiometric phase with Ca/Si molar ratio varying continuously between 0 and 1.67, and its actual composition at equilibrium is determined by minimizing the Gibbs free energy according to the dual-thermodynamic methods used by the GEMIPM2K model. The solid solution model for C–S–H is similar to that proposed by Kulik and Kersten [30]. Their original solid solution model was composed of two subsystems,

¹ Cement chemistry notation is used throughout, according to which C = CaO, S = SiO₂, A = Al₂O₃, and F = Fe₂O₃.

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