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Influence of multi-species solute transport on modeling of hydrated Portland cement leaching in strong nitrate solutions

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ABSTRACT

The differences between the predictions of Fickian diffusion and Nernst-Planck electro-diffusion based reactive transport models are investigated in the context of an important practical problem – leaching of Portland cement in strong nitrate porewater solutions under saturated conditions. Numerical results are presented for three distinct porewater solutions: deionized water, ammonium nitrate solution, and diluted porewater from a cementitious low-activity nuclear waste form. Solute concentrations predicted by the two transport models show significant differences: as much as a factor of two for ammonium nitrate leaching and as much as a factor of four for waste form leaching; whereas, negligible differences are observed for deionized water leaching. The major conclusion is that Fickian diffusion may be accurate enough for deionized water leaching, but electro-diffusion should be considered in the reactive solute transport modeling of ammonium nitrate decalcification and in the degradation modeling of cementitious materials exposed to nuclear waste form solutions.

1. Introduction

Understanding the fundamental mechanisms of ion transport is key to accurately assessing the long-term performance of cementitious materials exposed to aggressive solutions. Whether predicting the rate of decalcification, of ingress of chloride, or of release of radionuclides from a cementitious waste form matrix, there exists the need for describing solute transport; however, due to the presence of numerous ionic species in the pore solution and their reaction products, modeling solute transport in porous cements remains a challenging problem. Traditionally, transport phenomena in porous cementitious media have been described using the Fickian diffusion model with only a few chemical species and homogeneous reactions considered [1]. While accounting for the electrical coupling among diffusing ionic species is known to yield different results than diffusion modeling without electrical coupling, it is difficult to estimate a priori the qualitative and quantitative differences in results due to the nonlinear nature of reactive transport models. For the prediction of long-term performance of cementitious materials, it may be desirable to limit model complexity; however, it is important to understand the trade-off between model complexity and reliability. This article investigates the differences in solute concentrations predicted by these two distinct transport models, namely Fickian diffusion and electro-diffusion, and addresses a fundamental question: how is predicted solute transport affected by Coulombic interactions (electrical coupling) between the numerous ions in cement porewater solutions in the presence of strong nitrate external leachants?

The first model to describe solute transport in the absence of advection is attributed to Adolf Fick who, in 1855 [2], put forth the observation that a solute diffuses proportionally to its concentration gradient. Existing studies on leaching commonly employ the Fickian diffusion model to describe the transport of only a few rate-limiting ionic species without considering the entire chemistry and, thus, neglecting the physical constraint that the solution must remain locally electroneutral (see, for example [3]). Another common practice is to assume the diffusivity is the same for all the species in solution, which, when starting from an electroneutral initial condition, serves to maintain local electroneutrality [4–6]. Such practices are still employed because experimentally obtaining ion-specific Fickian diffusion coefficients may be both tedious and challenging because they may depend upon the system state, as evidenced by the large number of empirical concentration-dependent diffusion coefficients found in the literature [7–11]. In contrast, the Nernst-Planck (NP) electro-diffusion model provides a mechanism for maintaining local electroneutrality (in the absence of applied potential), and can account for some concentration-dependent diffusive behavior given an appropriate chemical activity model. The NP model has been adopted and amended by a number of disciplines, most notably for describing ionic transport in proteins [12–15], highly concentrated and ionic liquids [16–19], nanofluidic channels [20–23], and clays [24–29].

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For modeling transport in cementitious materials, the application of the NP model has gained popularity in recent decades. Samson and coworkers [30,31] employed the NP model to describe ion migration under an applied electric current during accelerated migration experiments. Other studies that applied the NP model to describe ion migration in cementitious materials can be found in [31–40], including two-phase models for unsaturated media [40]. Snyder and Marchand [41] carried out a unique experimental investigation of migration under a zero external potential in nonreactive porous frit exposed to various initial and boundary conditions; their findings indicated that simple Fickian diffusion could not adequately describe multi-ionic diffusion and in some cases the fitted value of the Fickian diffusion coefficient became negative, that is, a species was transported against its concentration gradient. Samson and Marchand [42] also found close agreement between their NP model results and experimental measurements of sulfate ingress fronts. Galíndez and Molinero [43] compared Fickian and NP model results of sulfate attack on cement paste using a limited number of ionic species and found that the NP model predicted the presence of near-surface gypsum front, whereas the Fickian model did not. Recently, Johanesson [38] compared two methods of solution of the NP model for a simple electrolyte solution. All these findings suggest that the Coulombic coupling of ions manifest in the NP model may be a significant factor in determining net ion transport rates. Indeed, a number of multiphysics transport models explicitly account for charge coupling [44–46]. Given that lifetime performance assessment of cementitious materials is based on the transport modeling of aggressive ionic species, a salient question is whether reactive transport behaviors predicted by the Fickian and NP models are substantially different in strong nitrate solutions, which has not been addressed previously. The motivation behind this study is to understand the tradeoff between computational complexity (Fickian vs. NP) and model reliability (or accuracy) by considering extensive homogeneous reactions between all possible solute species in the aqueous phase.

In this article, the Fickian diffusion and NP electro-diffusion based mass transport model results are compared within the context of a practical problem – aggressive leaching of a Portland cement in strong nitrate waste form solutions under saturated conditions; this condition is also relevant to interpeting testing carried out to assess decalcification of cements, which often is accomplished using concentrated ammonium nitrate solutions. While it may be more important to capture the chemical behavior [39], the aim here is to study only the differences between the Fickian and NP transport models for a given chemical system. To model the behavior of the chemical system accurately, we have included a total of 81 solute species that potentially form and provided all the relevant thermodynamic constants (see Appendices A and B). An empirical method is proposed for estimating the unknown ionic diffusion coefficients for the Nernst-Planck model, which are otherwise difficult to obtain from the literature (see Appendix C). To our knowledge, no studies exist in the literature that have considered the relevance of electro-diffusion in the presence of strong nitrate leachants. These comparisons are made using a single set of thermodynamic equations and parameters, which have been shown to yield a reasonable prediction of major constituent solubilities in unleached Portland cement [47]. The three aggressive leaching solutions considered herein, pertinent to testing and field performance conditions, are deionized water, ammonium nitrate solution, and diluted porewater solution from a simulated low-activity radioactive waste form; each of these leachants represents a distinctly different class of solutions: an infinitely dilute solution, a concentrated (≈ 1M) single-salt solution, and a concentrated (≈ 1M) multi-ionic solution, respectively. The investigation of these three solutions provides both a basis for determining the conditions for which the differences between the Fickian and NP models may be important and a means of gauging the uncertainties (or errors) stemming from the choice of transport model.

The remainder of this article is organized as follows. In Section 2, the geometry and conceptual model are outlined, and the governing equations and numerical approximation of the reactive transport model are detailed. Solution of the reactive-transport equations is realized through a two-step (staggered) iterative numerical approach that was developed by coupling an implicit finite difference (FD) solver in Matlab for both the Fickian and NP transport model formulations with the geochemical speciation solver LeachXS/ORCHESTRA [48]. In contrast to previous studies which employed an explicit FD scheme [25,28], the present work employs a fully implicit FD scheme in conjunction with the Newton-Raphson method to solve the nonlinear NP model equations; thus, allowing the use of arbitrarily large time step intervals with unconditional numerical stability. Section 3 presents the parameterization of the model including the aqueous and solid phase thermodynamic parameters necessary for calculating chemical equilibrium and, for the case of the NP model, the ionic diffusion coefficients. Previous studies considered only a few ions with known diffusion coefficients, because the diffusion coefficients for a large number of the ions are generally not available in the literature. Therefore, an empirical relationship is proposed for correlating the unknown ionic diffusion coefficients to both their formal charges and van der Waals volumes, as discussed in Section 3.3. Section 4 compares the Fickian and NP ionic transport models for four example cases, first within an inert porous medium and then within a reactive hydrated ordinary Portland cement (PC), considering the aforementioned three external leaching solutions. Section 5 recapitulates the major findings of each example case and summarizes their practical significance within the context of cementitious material leaching.

2. Models and methods

2.1. Simulation geometry

All simulations are performed at standard temperature and pressure for the one-dimensional case of a porous medium of length $\ell = 0.02$ [m], porosity $\phi_s = 0.20$ [m^3 connected porosity per m^3 total], and skeletal density of 2200 [kg/m^3]. A single face of the medium, at $x = 0$ is exposed to an external solution of infinite volume such that the concentrations at the specimen-solution interface are fixed (Dirichlet boundary). Concentrations are also fixed at the opposite face, at $x = \ell$, to the initial porewater concentrations (Dirichlet boundary). The choice of specimen length aims to capture the chemical changes which occur at the specimen-solution interface whereas the form of the right boundary condition is intended to mimic a large specimen which requires long times for depletion.

2.2. Reactive transport model formulation

In a saturated reactive porous medium, the 1D mass conservation expression must reflect the dissolution and precipitation reactions, that is,

$$\frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial x} - F_i \tag{1}$$

where $C_i(x,t)$ [mol/m^3] refers to the concentration of i^{th} species in the pore solution at spatial location x [m] and time t [s], and J_i [mol/m^2/s] is the flux of species i. The reactive rate term F_i [mol/m^3/s] accounts for a phase change of species i from the aqueous phase to a solid precipitate phase. Directly solving Eq. (1) is tedious because F_i depends simultaneously on C_i, requiring an iterative scheme which can be computationally expensive [1]. Therefore, in this work, the sequential non-iterative algorithm (SNIA) has been employed [42,49,50], which is a type of operator-splitting approach wherein the chemical equilibrium and transport equations are solved in a staggered manner. In the first step of the algorithm, the reactive rate terms are neglected in order to solve for the concentration at the next $(k+1)$ time step, $\widetilde{C}_i^{k+1}$, as given