



Coupling of chemical kinetics and thermodynamics for simulations of leaching of cement paste in ammonium nitrate solution



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ABSTRACT

A novel numerical method is proposed in this paper to model the leaching of various types of cement pastes in the ammonium nitrate solution by coupling chemical kinetics with chemical thermodynamics. Arrhenius equation and Eyring equation are applied to predict the rate constant of fast dissolution of portlandite in the ammonium nitrate, and a modified rate law is developed by incorporating the saturation ratio of the reaction. The estimations of leached depths from the proposed method comply with the well-known square root-time relationship and they also agree well with the reported experimental results. Moreover, the evolutions of porosity and major hydrate compositions during leaching are obtained. It is found that a simple linear relation exists for the acceleration factor of leaching in 6 M of ammonium nitrate with respect to leaching in pure water regardless of the type of the cement clinker.

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1. Introduction

Calcium leaching has long been recognized as a critical durability concern for the structures made of cementitious materials when subjected to aggressive environments [1–3], such as waste disposal systems, dams and underground infrastructures. In general, calcium leaching is a simultaneous process consisting of ionic transport, dissolution of calcium-bearing hydrates and changes of pore structures when the cementitious materials are in contact with the aqueous environments of low pH and calcium concentration [3]. Constant leaching of calcium can increase the porosity of the material leading to loss of integrity and strength. As a result, the material would be more vulnerable to the aggressive environments.

Leaching of cementitious materials in ammonium nitrate (NH_4NO_3) solution is an extreme case of leaching that can be found in the chemical plants, such as fertilizer manufactures [4]. Due to the weak acid nature of ammonium ion (NH_4^+) and the high solubility of calcium nitrate salt ($\text{Ca}(\text{NO}_3)_2$), leaching in such an environment is much severer and faster comparing to leaching in water. Nowadays, accelerated leaching test, i.e. leaching in the highly concentrated NH_4NO_3 solution instead of using pure water, has become popular [5–10]. The accelerated leaching could accelerate the leaching kinetics by two orders of magnitude with the same end products obtained as those leached in the water [9, 11]. Moreover, as demonstrated in the laboratory experiments where crystallization was prevented [4,5], the accelerated leaching was controlled by diffusion and the leached depth followed the square root-

time Relation (5), which is similar as the leaching in water. Accordingly, the overall degradation mechanism was often considered to be similar for both types of leaching. However, due to lack of experimental standards, the measured acceleration factors were widely scattered in the literatures and no consensus was found so far [2,4,5,9,10].

Comparing to the excessive numerical modelling of leaching in the pure water, the numerical study on leaching in NH_4NO_3 is limited. The chemical thermodynamic modelling technique was widely adopted in modelling the leaching in pure water [4,12,13]. However, it is not applicable in modelling the leaching in NH_4NO_3 . In particular, for the simulation of the accelerated leaching test, the pore solutions are generally undersaturated with respect to the dissolution of portlandite (CH), and thus the local equilibrium, which is assumed in the framework of chemical thermodynamics, does not apply.

Preliminary simulations of leaching in NH_4NO_3 solution were described by an empirical root-time relation [4,5]. The proportionality constant (a) in the root-time relation is required to be determined through specific experimental studies. Inspired by the successful applications of the solid-liquid equilibrium curve of calcium in modelling the regular leaching in deionized water, the equilibrium curve was further exploited in order to simulate the accelerated leaching [2,9,11,14]. The computations conducted using the equilibrium curve follows strictly the three-stage leaching scheme [2,9,11]. The solid content of calcium, represented by the solid content of CH and C-S-H, is solely determined by the dissolved calcium ion in the pore solution. The actual chemical reactions of other hydration products are usually ignored, which is different from the traditional method of chemical thermodynamics. Generally, the equilibrium curve for modelling the accelerated leaching was obtained by solubility experiment, which was carried out in a

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specific concentration of liquid environment at a certain temperature [11]. Therefore, it has certain limitations despite its simplicity and efficiency: (i) the experiments conducted with different test setups, such as concentration of NH_4NO_3 solutions, produced different equilibrium curves; (ii) this method generally assumed that CH and C-S-H were the only hydrates that would react and be leached; (iii) the application of equilibrium curve was confined, which could hardly be applied in the field problems where the multiple degradations and the crystallization due to wet-dry cycle were of high potential.

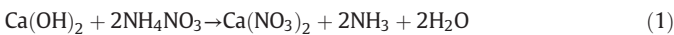
In this paper, a novel method is developed based on the basic chemical mechanisms to study the nature of the widely scattered acceleration factors. This method is applicable for the modelling of leaching in various concentrations of NH_4NO_3 solutions and field problems. By coupling the chemical kinetics and the chemical thermodynamics, chemical reactions of the major hydrates, CH, C-S-H, Aft, AFm and gypsum, can be evaluated simultaneously. In the present study, since advection and crystallization due to the wet-dry cycle are not considered, a simplified Poisson-Nernst-Planck (PNP) model is adopted to describe the ionic diffusion, and the operator splitting approach (OSA) is used to model the simultaneous diffusion-reaction process. The proposed method is applied to model various laboratory accelerated leaching tests on cement pastes in the highly concentrated NH_4NO_3 solutions. The estimations of leached depths are found to comply with the reported root-time relation and also agree well with the experimental measurements. Furthermore, the evolutions of porosity and major hydrate compositions during leaching can be obtained from the modelling. It is found that there exists a simple linear relation for the acceleration factor of leaching in 6 M of ammonium nitrate with respect to leaching in pure water regardless of the type of the cement clinker.

2. Coupling of chemical kinetics and thermodynamics

Recently, a module-oriented numerical method, which is comprised of three modules, i.e. an ionic diffusion module, a chemical reaction module and a damage evaluation module, has been developed by the authors [13]. This method is successful in simulating leaching in pure water and external sulfate attack by sodium sulfate solutions [13]. The developed chemical reaction module consists of the chemical thermodynamics only [13]. This module is extended, in this paper, by incorporating the chemical kinetics so as to consider the relationship between the undersaturated pore solution and the fast dissolution of CH in the presence of weak acid NH_4^+ . The proposed method is applicable for modelling leaching in various concentrations of NH_4NO_3 solutions as shown in Section 5. Moreover, by simply de-coupling the kinetics procedure, the method containing only the chemical thermodynamics can be easily applied to simulate the leaching in water [13].

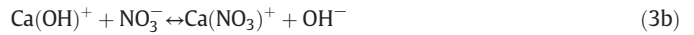
2.1. Application of chemical kinetics

The chemical equation for dissolution of CH in NH_4NO_3 solution is generally described by Eq. (1), which has been used by many researchers to account for the acceleration mechanism [2,9,15]. Due to the high solubility of $\text{Ca}(\text{NO}_3)_2$, the reaction constantly moves to the right and can hardly reach equilibrium. Some researchers also considered the ammonia (NH_3) to be a gaseous phase [15]. This argument is, however, controversial and thus is not considered in the present research.



In view of the weak acid nature of NH_4^+ , Eq. (1) actually proceeds in two steps, as given in Eq. (2). First, the weak acid NH_4^+ releases a hydrogen following Eq. (2a) [15]. Then the dissolution of CH is considered to proceed in an acidic environment and produces the complex ion $\text{Ca}(\text{OH})^+$, as described in Eq. (2b) [16]. In this environment, $\text{Ca}(\text{OH})^+$ would dissociate (Eq. (3a)) or the ionic exchange reaction

would take place when the concentration of nitrate ion NO_3^- is high (Eq. (3b)). Meanwhile, the equilibrium of water H_2O should always hold, see Eq. (3c).

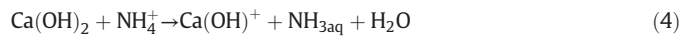


Due to the acidic environment, the complex ion $\text{Ca}(\text{OH})^+$ in the pore solution would continuously be consumed. Thus Eq. (2) could hardly reach equilibrium, and it is considered by the chemical kinetics. In terms of ionic complexation reactions shown in Eq. (3), their equilibriums are considered to be able to be reached in a short time span due to the high reaction rates [17]. These reactions are modelled by the chemical thermodynamics.

2.1.1. Activation energy and rate constant

The key of applying chemical kinetics is to obtain the activation energy of the reaction [18]. Activation energy is the “barrier” for any reaction to overcome before the reaction can proceed, as shown by E_a in Fig. 1. In the current case, to activate the dissolution of CH in acidic solution (Eq. (2b)), hydrogen is required to be extracted from Eq. (2a) first. Thus, two “barriers” have to be overcome. Consider the solid line to represent Eq. (2b) as the dissolution of CH in strong acid. The weak acid nature of the ammonium ion leads to higher activation energy, as shown by the dashed line. The increment of the activation energy is assumed to result from the dissociation reaction, i.e. Eq. (2a).

In this paper, the integrated chemical equation of Eq. (4), which is obtained by addition of Eq. (2a) and (2b), is modelled by the chemical kinetics. The activation energy for this integrated reaction is calculated from the elementary reactions in Eq. (2). In terms of the dissociation of NH_4^+ , i.e. Eq. (2a), the activation energy (E_{a1}) is related to the rate constant k_1 of the first order reaction by Eyring equation, given as Eq. (5) [19,20]. The rate constants k_1 for Eq. (2a) in various ambient temperatures were determined in the literature [18]. For the activation energy of dissolution of CH in the presence of hydrogen (E_{a2}), i.e. Eq. (2b), the value can be easily found in the chemical kinetics database [16]. The activation energy of the integrated reaction Eq. (4) is then assumed to be the summation of the activation energies from these two elementary reactions, as shown in Eq. (6). The rate constant for the integrated reaction is then calculated by using Arrhenius equation as given in Eq. (7) [21].



$$k_1 = \frac{k_B T}{h} e^{-\frac{E_{a1}}{RT}} \quad (5)$$

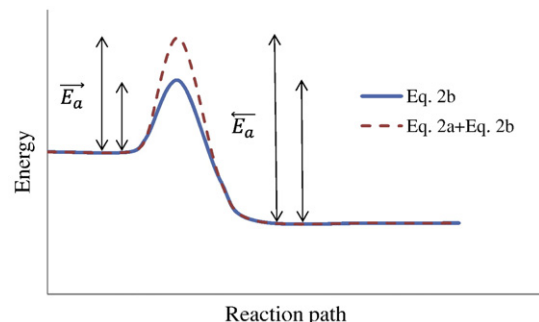


Fig. 1. Schematic diagram of change in activation energy.

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