



# Modelling the evolution of microstructure and transport properties of cement pastes under conditions of accelerated leaching



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## HIGHLIGHTS

- A 1D diffusion-based model for accelerated leaching of pastes in  $\text{NH}_4\text{NO}_3$  solution is developed.
- The transport of both calcium and nitrate is considered.
- The model enables to predict the changes in  $\mu$ -structure and transport properties due to leaching.
- Limestone filler reduces the degradation rate and changes in  $\mu$ -structure and transport properties.
- C-S-H leaching considerably contributes to changes in  $\mu$ -structure and transport properties.

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## ABSTRACT

Calcium leaching might be a significant degradation process in concrete and reinforced structures with an anticipated long-term service life such as nuclear waste disposal systems or large hydro structures (dams, bridges, water tanks). The leaching process is extremely slow under environmental conditions, which fosters the use of accelerated experimental approaches such as leaching in an ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) solution. In this paper, we develop a one-dimensional diffusion-based transport model with the purpose to predict the changes in microstructure and transport properties of saturated cement pastes in contact with a  $\text{NH}_4\text{NO}_3$  solution. The model helps to better understand the transient state of leaching which is difficult to observe by experimental work.

The main new elements in this model are change in model configuration with extended solution domains; ability to predict the spatial profiles of diffusivity and permeability; including the effect on solubility of the spatial-temporal evolution of nitrate concentration; and including the effect of limestone addition to the cement paste of leaching kinetics. This model is based on macroscopic mass balances for Ca in aqueous and solid phases which are linked together by applying a variable solid-liquid Ca equilibrium curve. Besides the prediction of the leached depth, porosity increase, portlandite and C-S-H contents, and the amount of leached Ca, the model also enables to estimate the variation of permeability and diffusivity over the domain at different immersion periods in  $\text{NH}_4\text{NO}_3$  solution. The model is verified by accelerated leaching experiments in 6 mol/l  $\text{NH}_4\text{NO}_3$  solution on CEM I cement pastes with/without limestone fillers. Verification with experimental results shows a good agreement.

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## 1. Introduction

A solution which is not in equilibrium with the cement phases, viz. a low pH or low alkaline solution, in contact with a cement

matrix will dissolve and leach cement constituents – a process known as leaching. In cementitious materials, calcium is the most significant ion for leaching because its concentration in cement is much higher compared to other potentially leachable ions and because of the high solubility of portlandite (CH). This process is also called decalcification. Under natural conditions, calcium leaching is an extremely slow process where a leaching front progresses with a speed of a few mm in hundreds of years [1]. Nevertheless, Ca-leaching is deemed as one of the most important long-term

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degradation processes in concrete [2], especially in systems with a long envisaged service life, such as nuclear waste disposal systems or hydro-structures (dams, bridges) or structures performing under aggressive environments where combined chemical attack can be more critical. Ca-leaching causes a change in cement mineralogy which results in a pH decrease [3] and change in porosity. pH decrease may induce rebar corrosion (although corrosion is at higher risk during chloride ingress and atmospheric carbonation [4]) while change in porosity leads to change in mechanical and transport properties of engineered structures.

To better understand leaching phenomenon and its effect on change of microstructure and transport properties, experiments have to be performed under accelerated experimental conditions given the slow nature of the process. Many accelerated methods such as applying an electrical field [5], using deionized water [6,7], using low pH solutions [8,9], applying flow-through conditions [10] or using high concentration ammonium nitrate solution [11,12] have been proposed to study the leaching process. Among these, using an ammonium nitrate solution to accelerate the leaching kinetics is one of the most used methods because it results in faster degradation compared to other methods under diffusive-transport conditions and has the same end-products.

As an alternative to obtain the physical properties of leached materials, modelling of the leaching process has also been pursued by many researchers. Nguyen et al. modelled the effects of Ca-leaching on the mechanical properties of concrete [13] and Bentz et al. considered the influence on the microstructure and diffusivity [14]. A 2D model was developed by Mainguy et al. to predict the degraded depth and the variation of leached calcium flux with time [15]. Jacques et al. developed a thermodynamic model to calculate the geochemical changes of concrete during leaching with rain and soil water types [3] and applied it to leaching under diffusive transport conditions accounting for change in transport properties [16]. Yokozeki et al. modelled the long-term behaviour of cementitious materials used in an underground environment [1]. Most of these models are based on the assumption of thermodynamic equilibrium of calcium in the solid and liquid phases in pure/deionized water which was first studied by Berner [17,18]. Recently, Wan et al. developed a solid-liquid equilibrium curve of calcium in ammonium nitrate solution [19] which was later used in his model [20].

Many modelling studies focus on the prediction of the degraded depth of leached materials and characterize its mechanical behaviour [21,22]. However, there are only a few studies which discuss the modification of the microstructure after leaching [23–25] and the effects of leaching on transport properties [26–28]. This study aims at strengthening and bridging the relationship between leaching degradation of cement paste, changes in transport properties (permeability and diffusivity), and microstructural modification by a numerical model. The current model is an extension of a previous version (described in [29]) by (i) accounting for the effect of limestone additions, (ii) removing the requirement to use measured Ca concentration in the surrounding solution as boundary conditions, and (iii) excluding the possibility of Ca precipitation by introducing a dependency of Ca solubility on nitrate concentration. The outcomes of the model are then verified with experimental results obtained from accelerated leaching experiments in a 6 mol/l ammonium nitrate solution on cement pastes with different w/c ratios with and without limestone fillers.

## 2. Model development for accelerated leaching in ammonium nitrate solution

### 2.1. Phenomenology and conceptual model

The proposed model is a one-dimensional diffusive transport model which aims at simulating leaching of saturated hardened

cement paste in contact with an aggressive  $\text{NH}_4\text{NO}_3$  solution. This model is based on a macroscopic mass balance for Ca in aqueous and solid phases. The model only considers the leaching of portlandite and calcium silicate hydrates which are the main hydrated phases in typical CEM I Ordinary Portlandite cement [30]. The hydration during leaching is not taken into account in the model because of the short duration of accelerated experiments. The outline of the proposed model is shown in Fig. 1.

### 2.2. Mathematical model

#### 2.2.1. Mass conservation of Ca

The mass balance equation for Ca in the pore solution is given as:

$$\frac{\partial(\phi C_{Ca})}{\partial t} - \frac{\partial}{\partial x} \left( D_{Ca}^e \frac{\partial C_{Ca}}{\partial x} \right) = - \frac{\partial C_{Ca}^s}{\partial t} \quad (1)$$

where  $\phi$  is porosity [-];  $C_{Ca}$  is concentration of Ca ion in pore solution [ $\text{mol}/\text{m}^3$ ];  $C_{Ca}^s$  is total concentration of Ca in solid phases [ $\text{mol}/\text{m}^3$ ];  $D_{Ca}^e$  is effective diffusivity of Ca ion [ $\text{m}^2/\text{s}$ ];  $t$  is time [s] and  $x$  is spatial distance [m].

#### 2.2.2. Porosity evolution

The total porosity  $\phi$  is expressed as follows:

$$\phi = \phi_0 + \Delta\phi_{CH} + \Delta\phi_{CSH} \quad (2)$$

where  $\phi_0$  is the initial total porosity which is experimentally determined or calculated as follows [31]:

$$\phi_0 = \frac{w/c - 0.17\alpha}{w/c + 0.32} \quad (3)$$

in which  $\alpha$  denotes the degree of hydration and  $w/c$  is water/cement ratio.  $\Delta\phi_{CH}$  is the porosity change due to portlandite dissolution:

$$\Delta\phi_{CH} = V_{CH}(C_{CH0} - C_{CH}) \quad (4)$$

where  $V_{CH}$  is molar volume of portlandite ( $33 \times 10^{-6} \text{ m}^3/\text{mol}$ ),  $C_{CH0}$  and  $C_{CH}$  are, respectively, the initial and current portlandite concentration [ $\text{mol}/\text{m}^3$ ].  $\Delta\phi_{CSH}$  is the porosity change due to change in C-S-H composition. The decrease in the Ca/Si ratio of C-S-H results in a reduction of the molar volume of C-S-H and consequent in a porosity increase.

$$\Delta\phi_{CSH} = C_{CSH}(V_{CSH0} - V_{CSH}) \quad (5)$$

where  $C_{CSH}$  is the concentration of C-S-H [ $\text{mol}/\text{m}^3$ ], and  $V_{CSH0}$  and  $V_{CSH}$  are the molar volume of the initial and current C-S-H, respectively. Data for the molar volume of C-S-H is still scarce and it is supposed to be a stoichiometry-dependent parameter. A recent experimental study [32] showed that the molar volume of C-S-H is proportional to the Ca/Si ratio,  $y$ , as:

$$V_{CSH0} - V_{CSH} = \omega(1 - y/y_0) \quad (6)$$

where  $y_0$  is the initial Ca/Si ratio of C-S-H,  $y_0 = 1.7$  [33], and  $0.02 < \omega < 0.04 \times 10^{-3} \text{ m}^3/\text{mol}$ . By comparing the porosity of leached and intact samples, we find that  $\omega = 0.04 \times 10^{-3} \text{ m}^3/\text{mol}$  gives the best fit. The Ca/Si ratio is calculated from the solid-liquid equilibrium curve (described later).

#### 2.2.3. Diffusion model

The effective diffusion model proposed by Garboczi [34] and adapted for leaching condition by Jain [7] is used to simulate the evolution of effective diffusivity of Ca in this model. This model, described by Eq. (7) is a modification of Garboczi's model, originally valid for hydration processes, to account for effects of leaching on the porosity-diffusivity relation because the same change in

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