



Quantification of leaching kinetics in OPC mortars via a mesoscale model

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HIGHLIGHTS

- A new 3D computational mesoscale framework to address calcium leaching kinetics.
- Captures the effect of aggregates and interface transition zone (ITZ) on leaching kinetics.
- Confirms the opposing influence of aggregates and ITZ in leaching kinetics.

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ABSTRACT

The problem of calcium leaching kinetics of ordinary Portland cement based mortars is revisited via a mesoscale approach. Based on state-of-the-art lattice-Boltzmann technique, a comprehensive suite of leaching analysis is undertaken to address a number of open questions such as (i) the competing effects of interface transition zone (ITZ) and aggregates, (ii) relative leaching rates of calcium between ITZ and mortar cement paste, and (iii) the influence of different water to cement ratios, volume fraction of aggregates and hence of ITZ on leaching kinetics. The mesoscale model is not only able to correctly reproduce experimentally observed trends but also confirm the commonly accepted hypothesis that ITZ and aggregates counter-balance their effect leading to similar portlandite leaching rates in cement paste and mortars. The model also confirms the applicability of simple scaling approach for upscaling leaching kinetics from pure cement paste to mortar scale under the condition that ITZ is fully percolated.

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1. Introduction

The importance of leaching of calcium (Ca) from cementitious materials due to exposure to aggressive water has long been recognized in studies concerning hydraulic structures [1] and nuclear waste disposal constructions [2–5]. The main questions are on the kinetics of leaching and its consequences on physical (porosity), transport (permeability, diffusivity), chemical (chemical retention) and mechanical properties (stiffness and strength) [6–9]. Experimental techniques have contributed crucially to fundamental process level understanding of the role of cement composition, water to cement (W/C) ratio, additives, fillers, volume fraction of aggregates, characteristics of the interfacial transition zone (ITZ), type of aggressive water, temperature, etc. on Ca leaching kinetics [10–14].

In OPC based mortars, the characteristics of ITZ are different to that of cement paste, with a higher W/C in ITZ and hence also higher effective diffusion coefficient and higher volume fractions

of portlandite (CH) and ettringite compared to the paste [15]. Furthermore, during leaching the ratio of effective diffusion coefficient of ITZ with respect to cement paste tends to gradually decrease, for instance, from about 2.5 for a sound mortar to around 1.4 for a partially leached mortar [15]. In spite of these differences between the two phases, the available experimental data suggest that CH dissolution front of pure cement paste and mortar are almost similar [15–17]. The above observation is specific to the mortar with higher volume fraction of aggregates and hence ITZ being close to or 100% percolated [10]. A common consensus reached is that ITZ, which is rich in CH and having higher porosity compared to mortar cement paste, allows preferential leaching of cement hydrates through it. This may lead to a higher leaching rate in ITZ compared to the mortar cement paste. On the other hand, the presence of sound aggregates tends to increase tortuosity of the mortar, thereby retarding the rate of leaching through the mortar cement paste. It is then hypothesized that these two effects counter-balance each other resulting in more or less similar extent of CH dissolution fronts in both pure cement paste and mortar [10,17]. Because there is no direct way to measure the influence of ITZ independent from the influence of the aggregates, the above hypothesis was first deduced by Bourdette et al. [10] based on pure

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diffusion experiments (no leaching) of mortar with various volume fractions of aggregates, V_{agg} (20%, 40%, 52% and 60%). They compared diffusivity of cement paste phase in mortar (i.e. cement paste and ITZ) with pure cement paste. The former cannot be directly measured and hence they use a theoretical approach to indirectly determine the quantity. They found that the diffusion coefficient of the cement paste phase in the mortar decreased with increase in V_{agg} up to 40%, but then increased by a factor of ≈ 1.75 at 52% and dropped further at higher V_{agg} . With this they concluded that the decrease in the diffusion coefficient of cement paste phase in mortar up to $V_{agg} = 40\%$ was attributed to tortuosity effect introduced by aggregates. Consequently, one should expect a slower leaching rate at $V_{agg} < 40\%$. The sudden increase at $V_{agg} = 52\%$ was attributed to percolated ITZ network, whose porosity was around 2.5 times more than that of mortar cement paste. From this they deduced that the leaching rate of cement paste phase in mortar at 52% is strongly influenced by the percolated ITZ network, which counter-balances the tortuosity effect resulting in more or less similar portlandite leaching front. The above analysis is also qualitatively valid if the diffusion coefficient of the cement paste phase in the mortar is transformed in terms of the effective diffusivity of the mortar for their experiments. Although the proposed hypothesis seems plausible, in a recent review by Patel et al. [18], with experimental evidence it was shown that the effective diffusivity of mortar monotonously decreases with increase in volume fraction of aggregates.

Therefore, further investigations seem justified based on the following missing elements:

- There is a need to provide additional arguments to explain the hypothesis concerning counter-balancing effect of ITZ and dilution effect of aggregates at full ITZ percolation.
- There are no data on the relative leaching rates of calcium between ITZ and mortar cement paste at various V_{agg} .
- There are separate studies on the influence of W/C ratios on leaching kinetics [13] and volume fraction of aggregates on effective diffusivity of chlorides on sound mortars [19,20]. These disparate studies can be combined to draw conclusions on the leaching kinetics of cementitious materials. However, there are no integrated quantitative analysis of the combined influence of different water to cement ratios, volume fraction of aggregates and thickness of ITZ on leaching kinetics within a single computational framework.

This paper aims to address systematically the missing elements via a new mesoscale leaching model. The term mesoscale here refers to a three-phase system comprising cement paste, ITZ and impermeable aggregates. At this scale, the behaviour of leaching kinetics can be better studied in each phase.

2. Mathematical/numerical model for calcium leaching

This section presents a formulation of boundary value problem for simulating calcium leaching at the mesoscale. The following key assumptions are made:

- Ca leaching results in the dissolution of mainly CH and C-S-H phases. Dissolution of CH and C-S-H phases occur instantaneously with CH preceding C-S-H dissolution based on equilibrium considerations. Other hydrated phases are ignored because of their low volume fractions as well as to simplify the conceptual model.
- Influence of ion activity and electro-kinetic charges on diffusion is neglected.

- Only total Ca and Si concentrations are considered as primary variables in the reactive transport model. It has been shown by the co-authors that considering these two components are sufficient to reasonably describe the dissolution of CH and C-S-H [21,22].

Under these assumptions, leaching at the mesoscale can be described by the following diffusion–reaction equation:

$$\partial_t(\phi(x)C^j(x)) = -\nabla \cdot \vec{J}^j(x) + R^j(x), j \in [Ca, Si] \quad (1)$$

$$\vec{J}^j(x) = -D_e(x) \nabla C^j(x)$$

where C^j is the aqueous concentration of j th chemical species [NL^{-3}], \vec{J}^j is the diffusive flux vector for j th chemical species [$NL^{-3}T^{-1}$], R^j represents the source/sink term due to dissolution [$NL^{-3}T^{-1}$], D_e is the effective diffusivity of chemical species [L^2T^{-1}] and ϕ is the total porosity [-]. D_e is defined via the following Archie's type expression:

$$D_e(x) = D_0 \phi^k(x) \quad (2)$$

where D_0 is the diffusivity of chemical species in capillary pore water [L^2T^{-1}], which is assumed to be same for both Ca and Si to ensure electro-neutrality. The exponent $k = 6$ was fitted based on a number of experimental data for sound hardened cement paste as shown in Fig. 1. The above Archie's model is similar to that obtained by Mainguy et al. [23], with the implicit assumption that the relationship also holds for leached cement paste. Moreover, the applicability of Archie's model for the effective diffusivity of cement paste is reviewed in Patel et al. [18].

The reaction term in Eq. (1) is computed as follows:

$$R^j(x, t + \Delta t) = \phi(x, t + \Delta t) \frac{(C_{eq}^j(x, t + \Delta t) - C^j(x, t + \Delta t))}{\Delta t}, j \in [Ca, Si] \quad (3)$$

where C_{eq}^j is the equilibrium concentration of j th chemical species [NL^{-3}]. Portlandite only contributes to the reaction term of Ca and the C_{eq}^{Ca} is taken as 19.48 mM for leaching with deionized water (computed using thermodynamic parameters in CEMDATA07

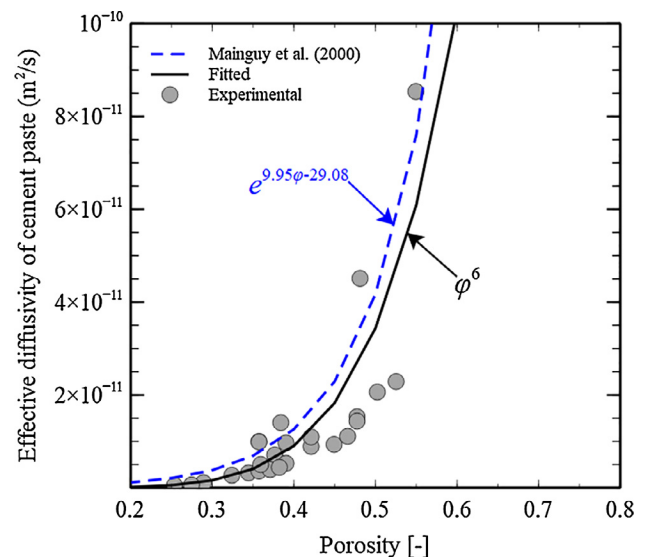


Fig. 1. Empirical model for effective diffusivity of hardened cement paste as a function of total porosity, fitted based on 24 experimental data points [18].

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