

Fundamental Reaction-Transport Model for Simulating Microstructure Development in Hydrating Cement Pastes

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A new stochastic microstructure model, called HydratiCA, is described that enables simulation of all the major chemical kinetic processes that occur in mineral-water systems: dissolution, solute transport, nucleation, and precipitation. An important feature of HydratiCA is that it is essentially free of empirical parameters, relying instead on kinetic and thermodynamic parameters that can, in principle, be experimentally measured. An important property of HydratiCA is its numerical convergence to the governing system of reaction-transport differential equations. The principles and main algorithms of the model are described briefly. The model is then applied to simulate the hydration of quick lime (CaO) in water to form calcium hydroxide. This example illustrates the operation of the major mechanisms involved in the hydration of hydraulic cementitious materials, and demonstrates the important relationships between microstructure development, kinetics, and thermodynamics of the system. The potential of the model as a research tool for investigating the early-age curing of hydraulic cements is discussed.

1. Introduction

Several microstructure-based models of portland cement paste hydration have been developed in the last two decades [1-4]. Although the different models are based on different starting assumptions, use different methods, and employ varying degrees of sophistication in the physicochemical description of the system, each has been successful at simulating aspects of the evolution of the three-dimensional (3-D) microstructure and physical properties.

As an example, the CEMHYD3D model [1,5] developed at the National Institute of Standards and Technology (NIST) is probably the most sophisticated of these microstructure models, at least in terms of the accuracy with which the starting microstructure is represented and the range of reactions that are considered. CEMHYD3D operates on 3-D digital images that capture many aspects of the microstructure, including the water-solids (w/s) ratio, the particle size and shape distribution, the volume and surface areas of each mineral phase, and the spatial distribution of these phases. CEMHYD3D defines probabilistic rules that are applied locally to mimic the processes of dissolution, through-solution diffusion, and nucleation and growth of hydration products. These rules

are empirically based, having been calibrated to experimental measurements made on ordinary portland cements to reproduce the major features of the evolution of the microstructure. In this sense, CEMHYD3D, like all the other microstructure models of cement hydration known to this author, is an interpolative model; its predictive accuracy is limited to cements that are similar to those with which it has been calibrated, and extending the model to include other materials is a matter of considerable effort.

Prominent alternatives to CEMHYD3D include the HYMOSTRUC model [2] developed at TU Delft and the IPK model [3] from EPFL. These models use different strategies for estimating the overall kinetics of hydration that are similar in spirit to the semi-empirical nucleation and growth models of Avrami [6,7]. These models also are interpolative because the semi-empirical parameters used in the assumed kinetic equations must be calibrated to experimental measurements of the rate of hydration. However, although HYMOSTRUC and IPK lack the structural sophistication and chemical differentiation of CEMHYD3D, their kinetic equations endow them with an intrinsic time scale that is absent in CEMHYD3D.

As a step toward an extrapolative microstructure model of hydration—one that is essentially free of empirical parameters and that can be applied equally well to a wide range of material systems—this paper describes an approach to reaction-transport modeling at the microstructure level that is complementary to, but differs significantly from, any of the aforementioned models of hydration. The advantage of this model, which is named HydratiCA, is that it simulates the local kinetics of each possible reaction using stochastic algorithms that are based on the statistical mechanical principles of transition state theory. Therefore, as the following sections will demonstrate, the model can track the dynamics of diffusion, nucleation, and chemical reactions in a unified way, free of empirical parameters and faithful both to the kinetics and thermodynamics of these varied phenomena.

2. Numerical Model

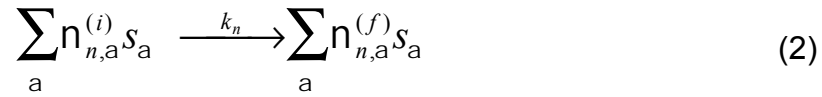
The HydratiCA model is based on stochastic algorithms for ideal diffusion of nonelectrolytes and homogeneous chemical reactions that were developed by Karapiperis and Blankleider [8]. HydratiCA extends those algorithms to include modeling of electrolyte diffusion and the details of heterogeneous reactions, including the kinetics of nucleation and growth of solids. These extensions to the original model of Karapiperis and Blankleider have been detailed in other papers [9,10], so only a brief description will be provided here.

The material microstructure is discretized on a regular cubic lattice with a lattice spacing λ . At each lattice site, a number of independent chemical agents may be located. These agents, called *cells*, each represent a fixed concentration of the material that they represent, and are endowed with all the properties of that chemical, including density, molar volume, self-diffusion coefficient at infinite dilution, specific heat, and internal porosity. The number of cells of a given chemical s_a at a lattice site is called the *occupation number*, N_a , of that chemical at the site. The set of occupation numbers of all cell types at each node is sufficient to fully characterize the microstructure.

Simulations of microstructure development are composed of a large number of cycles, each of which corresponds to some time increment τ . During each cycle, diffusion and reaction steps are executed in sequence. Diffusion is simulated as a random walk of the mobile cells on the lattice. The probability of displacing a given cell of type s_a to a nearest-neighbor site is

$$p = k_{D,a} \tau \quad (1)$$

where the diffusion rate constant $k_{D,a}$ is related to the effective diffusion coefficient of the species in the surrounding medium according to $k_{D,a} = D_a / l^2$ [8,9]. In the reaction step, any given reaction n can be written generically as



where $n_{n,a}^{(i)}$ and $n_{n,a}^{(f)}$ are the molar stoichiometric coefficients of species s_a as reactant and product, respectively, and k_n is the specific reaction rate constant, in units of mol/s for homogeneous reactions or mol/m²/s for heterogeneous reactions which occur at an interface between two phases. If p_n represents the probability that this reaction occurs once at a given lattice site, i.e. that $n_{n,a}^{(f)} - n_{n,a}^{(i)}$ cells of species s_a are created at the site during the reaction step, then the following expression for p_n as a function of the occupation numbers N_a ,

$$p_n = k_n \chi^{(\sum n_{n,a}^{(i)}) - 1} \frac{\tau}{l^q} \prod_b \max \left[0, \prod_{m=1}^{n_{n,b}^{(i)}} (N_b - m + 1) \right] \quad (3)$$

where θ is 0 for homogeneous reactions and is 1 for heterogeneous reactions, reproduces reaction kinetics that converge, as $\tau \rightarrow 0$, to the standard rate equation for reaction (2) [8,10]:

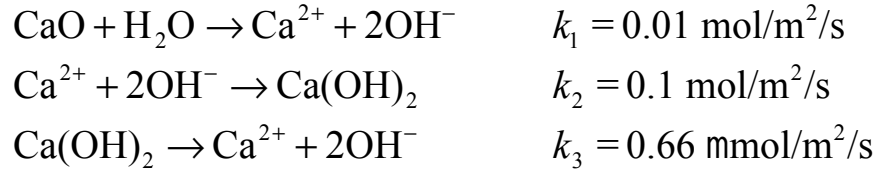
$$\frac{dc_a}{dt} = \left(n_{n,a}^{(f)} - n_{n,a}^{(i)} \right) k_n A_n^q \prod_b c_b^{n_{n,b}^{(i)}} \quad (4)$$

where c_a is the molar concentration of s_a . In Eq. (3), x is a constant that maps the ensemble average of occupation numbers to molar concentration (for solute) or volume fraction (for condensed phases). In Eqs. (1) and (3), therefore, we have a mathematical model which is numerically stable, which converges to the theoretical equations for the dynamics of the system at hand, and which is free of empirical parameters.

3. Results

The verification of the numerical algorithms, including numerical convergence to the standard reaction rate equations, nucleation kinetics, and diffusion of ionic species in solution, has been presented in detail in other papers [9,10]. Therefore, this paper will not consider the model verification but will proceed immediately to an illustration of its use for modeling cementitious materials.

Consider the hydration of quick lime, CaO, in water to form portlandite, Ca(OH)₂. Dissolution of CaO is assumed to be rapid and irreversible, while both dissolution and precipitation of Ca(OH)₂ are assumed to occur at finite rates:



The absolute value of k_1 is assumed here because it has not been found in the literature. However, the value of k_2 has been measured at room temperature by other researchers [11], and the value of k_3 was chosen so that $k_3/k_2 \equiv K_{sp} = 6.6 \times 10^{-6}$, as required by the principle of detailed balances at equilibrium, where K_{sp} is the solubility product of Ca(OH)₂. In this example, the initial system is a dispersion of 20 μm diameter digitized spheres of CaO in pure water, with CaO volume fraction of 0.51. The computational lattice is a cube with 50 sites in each dimension, and a lattice spacing of $\lambda = 4 \mu\text{m}$. The temperature is held fixed at 298 K. The molar volumes of CaO and of Ca(OH)₂ at 298 K are $1.69 \times 10^{-5} \text{ m}^3/\text{mol}$ and $3.31 \times 10^{-5} \text{ m}^3/\text{mol}$, respectively.

The microstructure development of this system is shown in Fig. 1 for two different scenarios that differ only in the details of the nucleation of

$\text{Ca}(\text{OH})_2$. On the left side of the figure, nucleation is assumed to occur heterogeneously on a single inert seed in the center of the lattice (not visible in the figure). On the right side, nucleation is assumed to occur on the surface of the dissolving CaO particles. The energetic barrier to nucleation is assumed to be the same in both simulations.

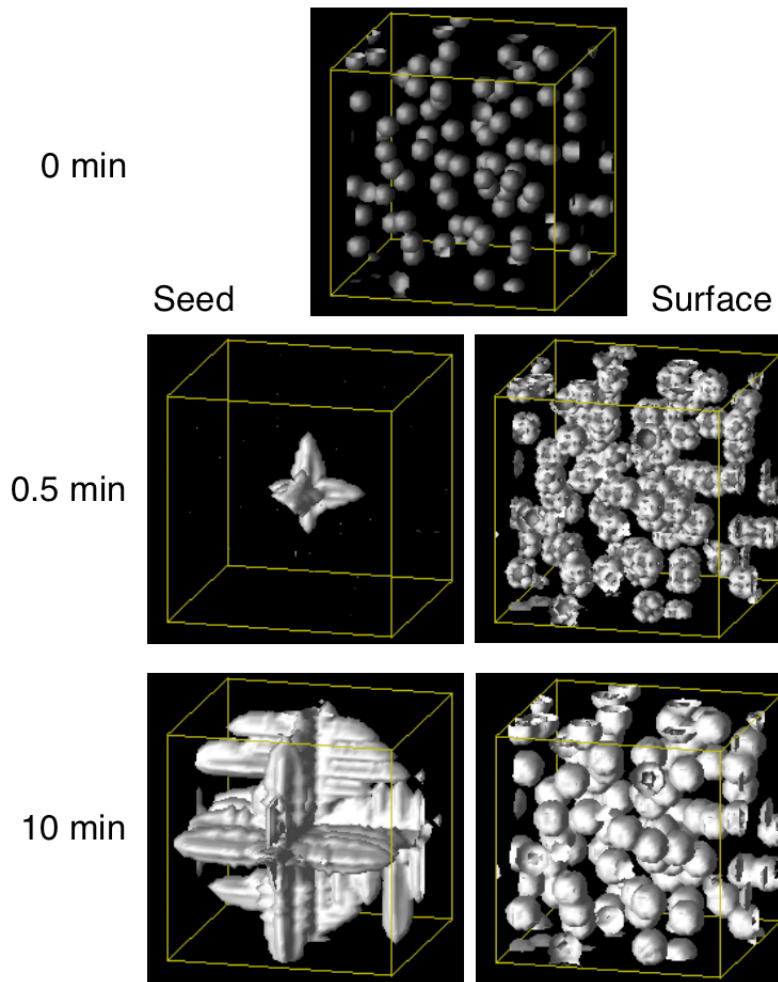


Figure 1 Simulated microstructure development as CaO particles dissolve in water and $\text{Ca}(\text{OH})_2$ nucleates either on a single inert seed (left) or on the surfaces of CaO (right).

It is clear from Fig. 1 that the nucleation mechanism is decisive in determining not only the kinetics of the reaction, but also the ultimate state of the microstructure. When nucleation occurs on a single seed in the liquid, the CaO particles continue to rapidly dissolve and provide fuel to the growing $\text{Ca}(\text{OH})_2$ crystal, such that the CaO particles have completely dissolved within 30 s. The $\text{Ca}(\text{OH})_2$ precipitate shown at 10 min is in thermodynamic equilibrium with the surrounding pore solution. In fact,

equilibrium was effectively achieved as early as 1.5 min. In contrast, when Ca(OH)_2 nucleates on the surfaces of CaO , the CaO particles are quickly covered with a continuous layer of Ca(OH)_2 . Again, Ca(OH)_2 continues to grow until it achieves equilibrium with the surrounding solution, but in this case the final equilibrium state is a metastable one, in which CaO remains at the core of the hydrated particles because it is protected from further dissolution by the impermeable Ca(OH)_2 layer.

The phase evolution and solution composition as a function of time for this system are shown quantitatively in Fig. 2. The top plot shows the time dependence of the volume fractions of CaO and Ca(OH)_2 , and the bottom plot shows the molar concentration of Ca^{2+} in solution. The seeded microstructure exhibits an increase in Ca(OH)_2 that follows a smooth sigmoidal curve, characteristic of first-order phase transformations occurring by classical nucleation and growth mechanisms [6,7]. Although not apparent in the plot, the first stable nucleus of Ca(OH)_2 forms at 2 s when the concentration of Ca^{2+} in solution is 151 mmol/L. The rate of growth of Ca(OH)_2 then increases rapidly between 2 s and 2 min due both to the increasing surface area of the precipitate and the increasing concentration of the solution as CaO continues to dissolve rapidly. After 2 min, the rate of growth decreases steadily as the solution becomes depleted in Ca^{2+} and OH^- (see lower plot of Fig. 2). For the unseeded microstructure, in which nucleation occurs on CaO surfaces, the first stable nucleus of Ca(OH)_2 forms by 0.1 s when the concentration of Ca^{2+} is 9.2 mmol/L. Thus the solution appears to be *undersaturated* with respect to Ca(OH)_2 when nucleation occurs. However, the concentrations are reported as an average over the whole solution, whereas the local concentration near the CaO surface is much higher, nearly 125 mmol/L, where nucleation first occurs. After the first nucleation event, the solution concentration continues to rise to a maximum value of 102 mmol/L after a time of 23 s. The maximum concentration is lower, and the subsequent decrease in concentration more rapid, in the unseeded microstructure than in the seeded one. One reason for the difference is that the volume fraction of Ca(OH)_2 , and therefore its surface area, is greater in the unseeded microstructure during the first minute of reaction, due to the larger number of nucleation sites. A second reason for the difference in kinetics is that the CaO surfaces become partially covered by a protective layer of Ca(OH)_2 , giving them less exposed surface area for continued dissolution.

For both the seeded and unseeded microstructures, the system converges to an equilibrium state in which the concentration of Ca^{2+} in solution is 11.81 mmol/L, which is indicated by the horizontal dashed line in the lower plot of Fig. 2. This concentration is equal to that predicted from the solubility product for Ca(OH)_2 if it is assumed that the activities $\{\text{Ca}^{2+}\}$ and $\{\text{OH}^-\}$ are equal to the molar concentrations $[\text{Ca}^{2+}]$ and $[\text{OH}^-]$, respectively.

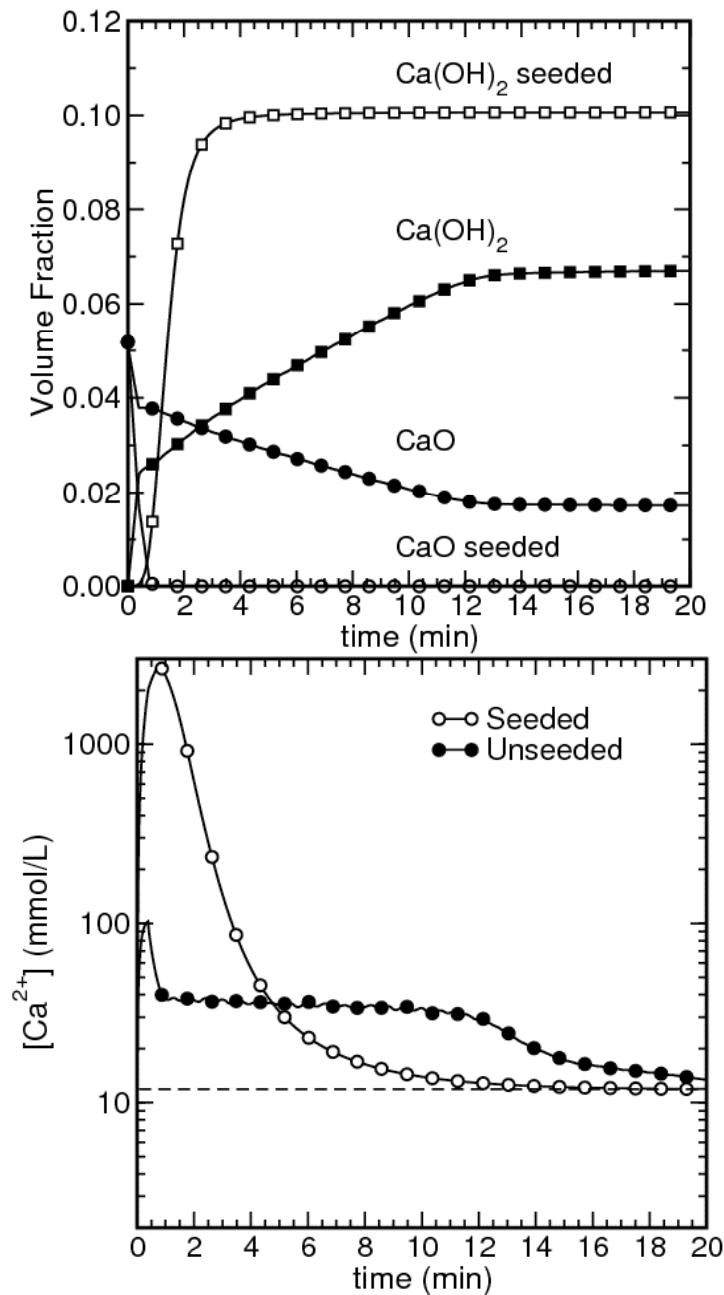


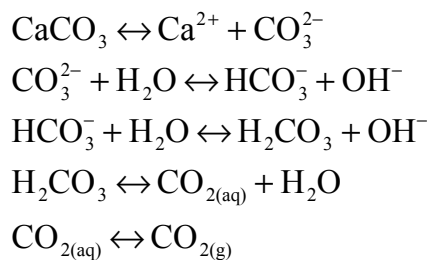
Figure 2 Volume fractions of CaO and Ca(OH)₂ (upper plot) and concentration of Ca²⁺ (lower plot) as functions of time for seeded and unseeded microstructures in Fig. 1.

If the simulations are repeated by using the extended Davies equation [12] to approximate the activity coefficients of these ions, then the model predicts an equilibrium concentration of Ca²⁺ of 19 mmol/L, which differs from the actual equilibrium of 22 mmol/L by 13 %. Even closer agreement to the true equilibrium concentrations could be achieved by using more accurate estimates of the activity coefficients.

At intermediate times, between 1 min and 10 min, the time dependence of the solid volume fractions in the unseeded microstructure is approximately linear (filled symbols in upper plot of Fig. 2), while the average solution concentration remains approximately constant (filled symbols in lower plot). This behavior indicates that the nutrients for continued growth of Ca(OH)_2 are being drawn, not from the bulk solution, but from freshly dissolved material immediately adjacent to the CaO surfaces. Thus, although growth occurs by a through-solution mechanism, it is almost indistinguishable from constant-rate topochemical conversion of CaO to Ca(OH)_2 at these intermediate times.

4. Discussion

The example of CaO hydration shown in the previous section is applicable to the production of slaked lime (Ca(OH)_2), which is an important industrial process in its own right. It is a matter of experimental inquiry to determine the correct rate parameters and nucleation energy to use as input to the model to achieve realistic predictions of the kinetics. This highlights the fact that, although the model is free of adjustable empirical parameters, it does require knowledge of the (measurable) properties of the materials and reactions that are to be modeled. Therefore, agreement between experiment and simulation can lead to confirmation that the correct rate parameters and reactions have been obtained in a given situation. For example, one may observe experimentally that carbonation is significant in the hydration of CaO , meaning that CaCO_3 , which is much less soluble than Ca(OH)_2 , forms in significant quantity. One could use this model to assess the potential for carbonation at a given partial pressure of CO_2 by simply augmenting the set of reactions in the input file with the appropriate series of reversible reactions for aqueous carbonates, such as



together with corresponding values of the rate constants and/or equilibrium constants.

The example of $\text{CaO}/\text{Ca(OH)}_2$ is also important because it embraces almost all of the relevant chemical and physical processes involved in the early-age curing of gypsum slurries and of hydraulic cements: dissolution of anhydrous phases, diffusion of ions in solution, and nucleation and

growth of hydration products. One should therefore expect the model to be a legitimate research tool for investigating the early-age behavior of such systems.

In the case of hydration of tricalcium silicate—itsself a “simple” chemical analog to the more complicated case of portland cement—there is some controversy over the precise mechanism(s) responsible for the well-known stages of rapid dissolution (0 min to 1 min), apparent “induction” period of slow reaction (1 min to a few hours), acceleratory period of increasing reaction rates (few hours to about 10 hours), and subsequent deceleratory period of decreasing hydration rates (after 10 hours) [13-19]. Especially at early ages, this system has proven difficult to probe with controlled experiments due to the extremely rapid changes that occur, the nonstoichiometry of the calcium silicate hydrate phase that is the major product of hydration, and the fact that much of the chemical changes occur at the surface of the dissolving particles and have relevant length scales in the nanometer range [16-19]. As a result, at least two theories of early-age hydration mechanisms for tricalcium silicate have been advanced [16-18], each of which may be *qualitatively* plausible but difficult to validate *quantitatively* against experimental results.

The key difference between these two theories of early-age hydration of tricalcium silicate is their proposed mechanism for the onset of the induction period which immediately follows a short period of extremely rapid dissolution of the solid. One theory [16] requires the rapid formation of a thin metastable layer of a type of calcium silicate hydrate (C-S-H(m)), which subsequently inhibits further dissolution of tricalcium silicate and which can achieve chemical equilibrium with the pore solution. Nucleation and growth of a more stable form of C-S-H perturbs this equilibrium by depleting the pore solution of calcium and silicate ions, thus destabilizing the metastable C-S-H(m) and causing its dissolution. As the C-S-H(m) layer dissolves, the tricalcium silicate layer is able to again dissolve more rapidly, marking the onset of acceleratory period. A second theory [17,18] proposes that the slow rate of dissolution during the induction period is caused by a kinetically slow step of detachment of hydroxylated ions from the surface of tricalcium silicate. According to this second theory, the quiescence in the system during an apparent induction period is caused not by chemical equilibrium with a metastable layer, but by a steady state condition in which C-S-H precipitates grow on the surface of tricalcium silicate at a rate which balances the rate of dissolution of hydroxylated tricalcium silicate.

The differences between these two theories are subtle, but they should have measurably different consequences for the solution composition, solid volume fractions, and microstructure development at early ages. The model described here is ideally suited to investigate these effects because

it is based on fundamental mechanisms of diffusion and reaction kinetics. Therefore, the assumptions of each of the two theories can, in turn, be adopted naturally within the model, and simulations can be performed using a range of reasonable values for the pertinent reaction rate constants. It should then be possible to determine which, if either, of these two prominent hydration theories can be made to agree with reliable experimental data. Precisely these kinds of simulations are now being performed, and the results should lend new insights into the early-age hydration behavior of silicate-based cements.

5. Conclusion

HydratiCA is intended to complement, not necessarily supplant, the microstructure models that already are available for simulating cement paste hydration. It captures fundamental aspects of diffusion and reaction kinetics in a way that provides a close link to measurable physicochemical parameters. The model has potential to differentiate some subtleties of the mechanisms of early-age hydration of tricalcium silicate and portland cement pastes. More than just an academic curiosity, the details of these mechanisms can have important implications for the tailoring of chemical admixtures to manipulate early-age behavior, and for understanding the complex interactions between different components of composite (blended) cements. And because it is a general model of diffusion and reactions based on the statistical mechanical principles of transition state theory, HydratiCA can be applied with equal validity to a wide range of aqueous mineral systems. It should be useful for simulating microstructure development during the hydration of gypsum pastes, for assessing the susceptibility of concrete to leaching and sulfate attack, and even for investigating alkali-silica reactions of concrete aggregates.

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