A REACTION-DIFFUSION MODEL FOR SIMULATING 3-D MICROSTRUCTURE DEVELOPMENT OF CEMENT PASTE

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Abstract
The early-age hydration of cement paste is governed by a number of coupled chemical reactions, all of which are mediated by dissolved species in the pore solution. To capture the fundamental kinetic aspects of hydration, a model is required that can accurately simulate the rate processes of electrolyte diffusion, dissociation, nucleation, and crystal growth. Moreover, such a model needs to be directly linked to the three-dimensional (3-D) microstructure development of the paste. If properly formulated, a suitable model should be able to simulate any one of a number of plausible hydration mechanisms, by which comparison to experimental data can be used to gain insight into the actual chemical kinetics. Such information can aid in development of tailored chemical admixtures for controlling the progress of hydration. This paper will describe a new 3-D reaction-transport model, called HydratiCA, that has been formulated for just such purposes. The model is based on cellular automaton algorithms for diffusion and chemical reactions that may be shown to converge numerically to the generalized diffusion equation for nonideal solutions and the standard rate equations for coupled elementary reactions, respectively. Examples will be shown of how the model can be used to assess the plausibility of alternate hypotheses for the onset of the acceleration stage of hydration of tricalcium silicate and for the early-age hydration kinetics of tricalcium aluminate/calcium sulfate pastes.

1.   INTRODUCTION

   Mathematical and computer models have been used for decades as research tools for investigating cement paste hydration, and it is not hard to see why. Several types of complexity, inherent in the hydration process, act to confound a careful experimental examination of the underlying processes, and render it virtually impossible to make detailed predictions of hydration behavior without some kind of a model to interpret experimental data. One of these complexities is the three-dimensional (3-D) microstructure of the paste, which has important features ranging from nanometers to hundreds of micrometers and, more importantly, which continually evolves in time. The geometry of the microstructure and arrangement of the phases in it, especially the porosity, can dramatically influence the kinetics of hydration. A second complexity is that hydration is not a single chemical reaction, but instead consists of a rather large number of coupled chemical reactions that are mediated by transport in the pore solution. The full set of chemical reactions has not been characterized in

detail, and there are still debates in the literature over the correct set of reactions for a given cement system as well as the rate-controlling mechanisms that govern the overall kinetics.

The microstructural aspect of cement paste hydration has been addressed in a number of computer models, beginning with the pioneering work of Jennings and Johnson[i] and including the HYMOSTRUC model developed at TU Delft[ii] and the CEMHYD3D model developed at NIST[iii]. These models have advanced our understanding of the microstructural changes that occur during hydration, and they have successfully predicted a number of properties of cement paste that depend on the capillary pore system. Nevertheless, these models often do not fully address the chemical complexity of the hydration process, and this limits their ability to simulate kinetics, to capture the effects of chemical admixtures, or to address the compositional variability that is observed in hydration products such as C-S-H[1] and ettringite.

This paper describes a new computer model, called HydratiCA, that has been designed to accommodate complexity both in 3-D microstructure and in the description of the chemical reaction kinetics. The model is described very briefly in the next section; more details can be found in other papers[iv,v]. Afterward, the model is applied to investigate the rate-controlling mechanism of tricalcium silicate hydration. Finally, the use of HydratiCA to investigate the hydration of tricalcium aluminate and Portland cement will be discussed.

2.   MODEL DESCRIPTION

Within HydratiCA, hydration kinetics are modeled by considering the individual fundamental chemical reactions that occur, according to accepted principles of chemical kinetics and transition state theory. The necessary kinetic parameters of each reaction can be measured in a laboratory once for each mineral of a given composition—admittedly a challenging task—and then used to model any cement mix design equally well without further calibration, provided that the cement itself is adequately characterized. This approach recognizes that there are only four primary rate processes governing the structural changes in cement paste: (1) dissolution and growth of mineral phases, (2) diffusion of mobile species in solution, (3) complexation reactions among species in solution or at solid surfaces, and (4) nucleation of new phases. The kinetics of all four of these basic processes are unified by the principles of transition state theory (TST)[vi].

According to TST, any observable rate process can be described in terms of a free energy surface. If the entropy of activation is assumed independent of temperature, then the rate constants for a reaction in the forward and reverse directions are

$$k_+(T) = k_+(T_0)\exp\left[\frac{-\Delta H_+^*}{k_B}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad , \quad k_-(T) = k_-(T_0)\exp\left[\frac{-\Delta H_-^*}{k_B}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{1}$$

where T_0 is the reference temperature at which the values of the rate constants are known, and ΔH_+^* and ΔH_-^* are the activation enthalpies for the forward and reverse processes, respectively, and ΔH_{rx} is the enthalpy of reaction. It is important to recognize that the rate constants in Eq. (1) are absolute rate constants for the elementary reaction in question, not the net rate constant that would be readily measured in a laboratory. The latter quantity will

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[1] Cement chemistry notation is used throughout this paper, e.g. C = CaO, S = SiO_2, A = Al_2O_3, H = H_2O.

depend on the instantaneous quantity of reactants and how far the reaction is from equilibrium when the measurement is made. However, by keeping track of both the forward and reverse rates for a given elementary reaction using Eq. 1, one can simulate the net rate of the reaction, regardless of the concentrations of each substance at any particular moment. In particular, if the reaction is at equilibrium, then the forward and reverse rates must be equal, which implies that their ratio equals the equilibrium constant for the reaction. In this way, TST provides an explicit link between the rates of reaction (chemical kinetics) and the equilibrium state (thermodynamics). Furthermore, because k_+ and k_- depend on temperature according to Eq. 1, this approach provides the dynamic basis for the temperature dependence of the equilibrium constant, known as the van't Hoff relation[vii]. Thus, a complete dynamic description of local kinetics and equilibria over a modest temperature range is given by values for k_+ and k_- at a reference temperature (or only one rate constant when K_{eq} is known), together with the activation enthalpy in either direction and the net enthalpy of the reaction.

The details of how these kinetic principles are incorporated and tied to microstructure development do not fit within the scope of this paper, but the reader may obtain a complete description in other papers[iv,v]. In brief, a cubic 3-D lattice is defined with spacing λ between lattice sites. The initial cement paste microstructure is mapped onto this lattice by assigning a phase (e.g. tricalcium silicate, tricalcium aluminate, gypsum, water, etc) to each lattice site. These materials are themselves finely discretized into small quanta of concentration called cells; the number of these cells of a given material at a particular lattice site determines its concentration there, and multiple materials may be present at a given lattice site.

Transport of solute species is simulated by allowing each cell at a lattice site to execute a random walk to a neighboring site, the probability of the walk depending on the intrinsic mobility of the cell at the site and the length of the time increment being considered. The probabilistic rule that is used is formulated to accurately reproduce the kinetic laws of diffusion or advection[iv]. Similarly, any given chemical reaction at a lattice site is simulated by a probabilistic rule, in which the probability of the reaction occurring depends on the reaction rate constant and on the numbers of cells of each reactant that participates in the reaction[v]. The microstructure evolves automatically as the model updates the types and numbers of cells at each lattice site in the system for a small time increment, and then the whole cycle is repeatedly executed to simulate longer times.

This input includes the necessary information for each fundamental reaction that can occur (rate constant, activation energy, nucleation energy barriers, and stoichiometry) as well as the intrinsic mobilities of each diffusing solute species. In addition to the reaction parameters, several properties of each of the constituent substances are also required. For simple condensed phases, the density (ρ), molar volume (V_m), and, for non-isothermal simulations, the isobaric heat capacity (C_p) must be supplied. For mobile solute species, one must supply the electrical charge (z), the diffusion coefficient at infinite dilution in water, (D_0) and ion-specific parameters necessary to calculate the activity coefficients[viii]. Values for many of these properties can be found in textbooks or other reference materials[ix,x]. For solids that can exhibit a range of chemical compositions (such as C-S-H), the model handles the compositional variability by a solid solution approximation using stoichiometric end members to encompass the range of compositions. Each end member is assigned values for all the properties just enumerated, and then the relative rates of formation of each member at a lattice site determine the local composition and properties of the phase.

Although a number of fundamental parameters are required for input, there is no explicit dependence on mix design or cement clinker composition. In other words, one of the powerful motivations for developing this kind of model is that one does not need to adjust any of the reaction parameters to simulate different mixes. Instead, the differences between mixes, such as water-solids ratio, clinker composition, and particle size distribution, are specified at the beginning of the simulation through the assignment of the cell types and numbers at each lattice site.

3.   RESULTS AND DISCUSSION

In this section, HydratiCA is applied to investigate the reaction kinetics involved in the hydration of tricalcium silicate (C_3S). The general kinetic features of C_3S hydration are well-established and are shown in Fig. 1. The rate is extremely large for the first minute after wetting (Stage 1), but rapidly diminishes to a low rate during the induction period (Stage 2). After some time, the rate gradually accelerates (Stage 3) to a maximum value but afterward decreases continuously and remains low thereafter.
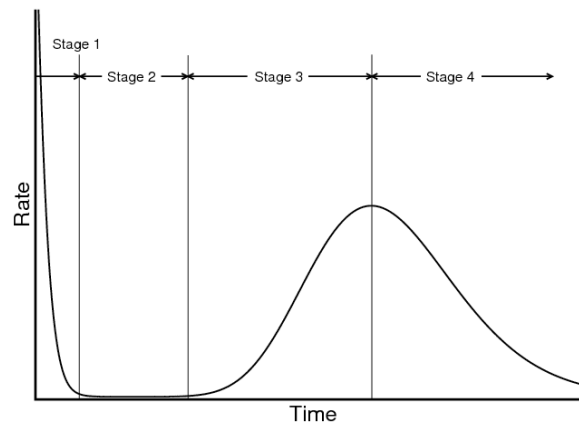

Figure 1. General progress of the rate of hydration of C_3S as a function of time, redrawn from Ref. [xi].

The mechanism(s) by which the rate rapidly decreases at the end of Stage 1 but increases at the onset of Stage 3 has been a subject of debate for many years. On one hand, there is wide agreement that the rate acceleration in Stage 3 is controlled by growth of a calcium-silicate-hydrate phase (C-S-H). The controversial aspects are (1) what causes the rate reduction at the end of Stage 1, and (2) why does the surrounding solution maintain a nearly constant composition until the end of Stage 2. One theory[xi], here called the **equilibrium theory**, is that a thin layer of a metastable hydrate (C-S-H(m) in this paper) forms a semipermeable barrier layer on C_3S surfaces in Stage 1 and severely limits the rate at which dissolution of C_3S occurs in Stage 2. By this theory, the nearly constant solution composition is due to near equilibrium conditions between the solution and the barrier layer. Hydration rates accelerate at the end of Stage 2 due to the nucleation and growth of a more stable form of C-S-H at the expense of the protective layer. An alternative theory[xii], here called the **steady-state theory**, is that the reduction in hydration rate in Stage 1 is due to hydroxylation of C_3S surfaces and the surface adsorption of calcium ions from solution. By this theory, a stable form of C-S-H nucleates within seconds after wetting, and the nearly constant solution composition in Stage

2 is due to a steady-state condition between dissolution of C_3S and growth of C-S-H. Both theories agree that growth of C-S-H is rate-controlling in Stage 3 and that the accelerating rate of hydration in Stage 3 is therefore due to the increased surface area of C-S-H.

In the space available here, HydratiCA is applied to demonstrate the mere plausibility of the equilibrium theory just described. Table 1 shows the materials and material properties that were used for the simulations. Most of the values used can be found in standard textbooks[ix,x] or research papers[xiii,xiv]. Note in particular that, in addition to the metastable C-S-H(m), two different types of C-S-H are defined. These differ principally in their Ca/Si molar ratios, and both are needed to capture the compositional variability in C-S-H that is experimentally observed as a function of the calcium concentration in solution[xii].

Table 1 Material properties and reaction rate constants used in HydratiCA to model hydration of C_3S. ρ is the density, V_m is the molar volume, the transport factor is defined to be the diffusion coefficient of mobile species in the material divided by their mobility in water, D_o is the diffusion coefficient at infinite dilution, k_{diss} is the forward rate constant for dissolution in water, and K_{sp} is the solubility product of the material. Superscripts on values indicates the source of the value. Where values are not given they are either not meaningful or were not used in the simulations.

Material/Ion	Formula	ρ (kg/m³)	V_m (10^{-6} m³/mol)	Transport Factor	D_o (10^{-9} m²/s)	k_{diss} (10^{-6} mol/(m²·s))	Log K_{sp}
H_2O		1000	18.1	1.0	3.0[x]		
Ca_3SiO_5	C_3S	3210[ix]	72.4[ix]	0		10.0[xv]	0.477[xvi]
C-S-H(m)	$C_3S_2H_3$	1750	100.0	0.001		0.29	-17.14
C-S-H(I)	CSH_4	2200[xiv]	85.7	0.01		0.16	-6.92
C-S-H(II)	C_2SH_5	1850[xiv]	161.2	0.75		0.019	-11.84
$Ca(OH)_2$		2240[ix]	33.08[ix]	0		32.3[xvii]	-4.37[xvii]
$Ca^{2+}_{(aq)}$					0.72[x]		
$OH^-_{(aq)}$					5.28[x]		
$H_2SiO_4^{2-}_{(aq)}$					0.70[x]		

The left plot of Figure 2 compares the results of HydratiCA simulations of C_3S hydration (solid curves) with experimental observations made on C_3S suspensions[xii] (discrete points) in which the concentration of calcium in solution is held fixed at either 11 mmol/L or 22 mmol/L. The agreement is quite good in both cases. In particular, when the calcium concentration is 11 mmol/L, the model correctly predicts both a great reduction in the induction period and the lower hydration rate at later ages relative to the system at 22 mmol/L calcium. The duration of the induction period at 22 mmol/L also is approximately correct. The uncertainty in the experimental measurements, for example the accuracy with which the calcium concentration in solution was fixed, has not been reported, so it is difficult to make any more detailed quantitative comment on the goodness of fit. The left plot in Fig. 2 also shows the simulated degree of hydration when the calcium concentration in solution is allowed to vary freely (dashed curve labeled "Unconstrained").

For the same simulated systems, the right plot in Fig. 2 shows the predicted and measured time dependence of silicate concentration in solution. The predicted trends are qualitatively consistent with the experimental observations, although measured concentrations are two or three times greater than the predictions. It should be remembered that the measured
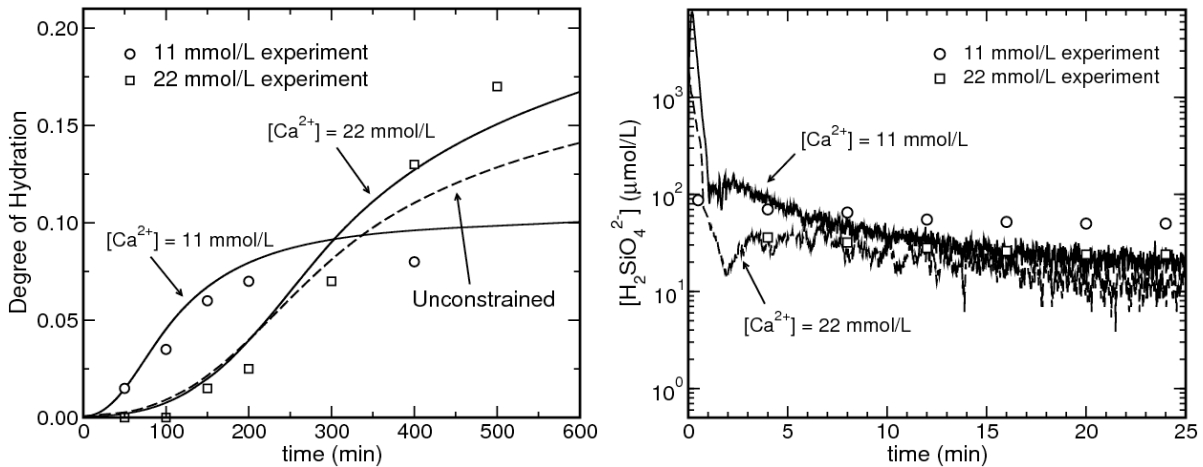
Figure 2. Simulated degree of hydration (left) and concentration of silicates in solution (right) of a C₃S paste with water-solid mass ratio of 0.5 and a solid surface-volume ratio of 0.29 μm⁻¹. Open circles and squares are experimental measurements reported in Ref. [xii] for calcium concentrations of 11 mmol/L and 22 mmol/L, respectively.

silicate concentrations are very low in any case, on the order of a few tens of μmol/L with an unknown degree of certainty. In any case, the observed large decrease in silicate concentration in the first few minutes is captured by the model.

Because two variants of C-S-H are able to form during hydration, the average composition of C-S-H in the microstructure is a pseudo-continuous quantity that can freely change depending on the chemical potential of solute species at the growth sites. Figure 3 shows the predicted Ca/Si molar ratio of the C-S-H phase when the calcium concentration is fixed at 11 mmol/L or 22 mmol/L. The predictions are consistent with at least two pieces of experimental evidence. First, the Ca/Si molar ratio is known to be lower when C-S-H is grown in solutions with low calcium concentrations than when it is grown in solutions saturated with respect to Ca(OH)₂ (roughly 22 mmol/L total calcium)[xiii]. Second, the volume-averaged Ca/Si molar ratio in pastes of C₃S is often reported to be near 1.7 after several hours or days of hydration, which is the value approached by the upper two curves in Fig. 3. Therefore, the simple two-end-member model of C-S-H composition appears to capture the compositional variation of that phase adequately.

This modeling study is intended to demonstrate the plausibility of the equilibrium theory of early-age hydration of C₃S. HydratiCA is able to simulate microstructure development and chemical kinetics in a more fundamental and detailed way than any previous model. Thus, the model has demonstrated for the first time the consistency of the equilibrium theory with both the kinetics of C₃S hydration and the compositional variability of C-S-H. Of course, the plausibility of the equilibrium theory does not rule out the steady-state theory, and more research is needed to adquately test the steady-state theory with HydratiCA. However, to date, the author has not been able to discover a set of coupled reactions and associated rate parameters for implementing the steady-state theory by which the model is able to agree, even qualitatively, with the experimental data cited here[xii–xiv].
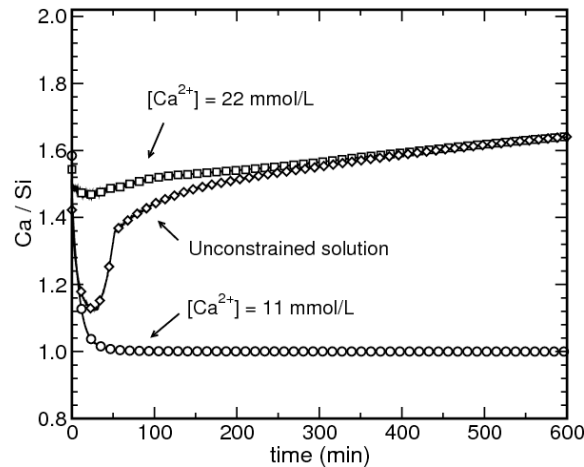
Figure 3. Predicted Ca/Si molar ratio of C-S-H formed from C₃S when the calcium concentration in solution is fixed at 11 mmol/L, fixed at 22 mmol/L, or is unconstrained.

The approach to modeling taken here is general, and it can accommodate a wide range of simultaneously coupled reaction and transport phenomena if the model is given the correct kind of input. For example, HydratiCA is currently being used to investigate the mechanism of hydration of tricalcium aluminate (C₃A) with and without gypsum additions. This work is still in preliminary stages, but so far has indicated that ettringite may not convert immediately to monosulfate when gypsum is exhausted from the system. In the past, ettringite was thought to form a protective layer around C₃A grains, controlling the otherwise extremely rapid hydration of that phase and preventing flash set. By this line of thinking, the observed rapid increase in C₃A dissolution rate, which coincides with the time at which gypsum is exhausted, was assumed to be caused by conversion of ettringite to a monosulfate phase. The preliminary results using HydratiCA suggest that the ettringite → monosulfate transformation may not be rapid enough to explain the changes in hydration rate when gypsum is consumed. This suggestion also supports recent experimental work by Minard et al[xviii], which indicates that adsorption of sulfate ions on C₃A surfaces, and not a layer of ettringite, may be responsible for the reduction in C₃A dissolution rates.

4.   SUMMARY AND PROSPECTUS

This paper has described a new fundamental model of microstructure evolution in aqueous mineral systems. The model, called HydratiCA, provides detailed, fundamental descriptions of both chemical kinetics and 3-D microstructure development. When applied to simulate the early-age hydration of C₃S, the model confirms the plausibility of the equilibrium theory for early-age hydration, but does not at this time rule out the steady-state theory. HydratiCA is being extended to include tricalcium aluminate/gypsum systems and, eventually, ordinary Portland cement pastes. The generality of the model formulation also will enable it to be applied to concrete degradation phenomena (sulfate attack, alkali-silicate reactions, etc.).

REFERENCES

[i] Jennings, H.M. and Johnson, S.K., "Simulation of microstructure development during the hydration of a cement compound," *J. Am. Ceram. Soc.* **69** [11] 790-795 (1986).

[ii] van Breugel, K., "Simulation of hydration and formation of structure in hardening cement-based materials," Ph.D. thesis, Delft University of Technology, Delft, The Netherlands, 1991.

[iii] Bentz, D. P., "Three-dimensional computer simulation of cement hydration and microstructure development," *Journal of the American Ceramic Society*, **80** [1] 3-21 (1997).

[iv] Bullard, J. W., "Approximate rate constants for nonideal diffusion and their application in a stochastic model," *Journal of Physical Chemistry A*, **111** [11] 2084-2092 (2007).

[v] Bullard, J. W., "A three-dimensional microstructural model of reactions and transport in aqueous mineral systems," *Modelling and Simulation in Materials Science and Engineering* **15** 711-738 (2007).

[vi] Glasstone, S., Laidler, K.J., and Eyring, H. *The Theory of Rate Processes*. McGraw-Hill, New York, 1941.

[vii] Van't Hoff, H. *Vorlesungen über Thoretische und Physakalische Chemie*. Braunschweig, Berlin, Germany, 1903.

[viii] Harned, H.W. and Owen, B.B. *The Physical Chemistry of Electrolytic Solutions. 3rd Edition*. Reinhold Publishing, New York, 1958.

[ix] Taylor, H. F. W. *Cement Chemistry, 2nd Ed.*, Thomas Telford, London, 1997.

[x] Mills, R. and Lobo, V.M.M. *Self-Diffusion in Electrolyte Solutions*. Elsevier, Amsterdam, 1989.

[xi] Gartner, E. M., and Gaidis, J. M., "Hydration mechanisms, I," *Materials Science of Concrete*, The American Ceramic Society, Westerville, OH, 95-125, 1989 (and references therein).

[xii] Garrault, S., and Nonat, A., "Hydrated layer formation on tricalcium and dicalcium silicate surfaces: Experimental study and numerical simulations," *Langmuir* **17** 8131-8138 (2001).

[xiii] Garrault-Gauffinet, S., and Nonat, A., "Experimental investigation of calcium silicate hydrate (C-S-H) nucleation," *Journal of Crystal Growth* **200** 565-574 (1999).

[xiv] Jennings, H.M, "A model for the microstructure of calcium silicate hydrate in cement paste," *Cement and Concrete Research* **30** 101-116 (2000).

[xv] Damidot, D., Bellmann, F., Möser, B., and Sovoidnich, T., "Calculation of the dissolution rate of tricalcium silicate in several electrolyte compositions," *Cement-Wapno-Beton* **12/74** [2] 57-67 (2007).

[xvi] Parkhurst, D.L., "User's guide to PHREEQC---A computer program for speciation, reaction-path, advective-transport and geochemical calculations," Water-Resources Investigations Report 95-4227. U.S. Geological Survey, 1995.

[xvii] Tadros, M.E., and Skalny, J., and Kalyoncu, R.S., "Kinetics of calcium hydroxide crystal growth from solution," *J. Colloid Interface Sci.* **55** [1] 20-24 (1976).

[xviii] Minard, H., Garrault S., Regnaud, L., and Nonat, A., "Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum," *Cement and Concrete Research* **37** [10] 1418-1426 (2007).