

Microstructure models of cement: their importance, utility, and current limitations

Shashank Bishnoi^{1*}, Jeffrey W. Bullard²

¹ Department of Civil Engineering, Indian Institute of Technology Delhi, India

² Department of Materials Science & Engineering, Texas A&M University, USA

Received: 17 November 2021 / Accepted: 07 June 2022 / Published online: 27 June 2022

© The Author(s) 2022. This article is published with open access and licensed under a Creative Commons Attribution 4.0 International License.

Abstract

Microstructure models seek to explain or predict various material properties in terms of the structure or chemical composition at scales of several hundred nanometres to several hundred micrometres. Such models therefore bridge the scaling gap between atomistic models and continuum methods, and consequently can help establish and validate scaling relations across those scales. Microstructure models have been applied to cementitious materials for at least four decades to help understand setting, strength development, rheological properties, mechanical behavior, and transport properties. This letter describes the current state of cement microstructure modelling in several areas that are important for engineering. It is not meant to be an exhaustive review, instead highlighting the kinds of models that can now be applied to different aspects of cement binder behaviour. Special attention is paid to challenges or limitations of each kind of model. This is done to promote the judicious use and interpretation of models and especially to indicate where future research could make inroads on problems that are currently inaccessible to microstructure models.

Keywords: Cement; Concrete; Microstructure; Modelling; Hydration

1 Introduction

Concrete derives most of its engineering properties from the hydrating cement microstructure. Sophisticated techniques like electron microscopy and nuclear magnetic resonance spectroscopy continue to improve our understanding of cement microstructure, but translating those structural characteristics to engineering performance is still a difficult proposition. High-fidelity models of the material composition and structure, which bridge the length and time scales of interest, can potentially help interpret experimental observations and guide the development of structure-property relationships for concrete. Within the set of available model types, microstructure models are defined here as numerical models that explicitly simulate the composition and structure at length scales of nanometers to millimeters, often as the microstructure evolves in time. Phase field [1-3] and Q-state Potts models [4-6] are examples that have been widely applied to rigorously simulate solidification, sintering, and grain growth in metals and ceramics for which the composition, thermodynamics, and crystal structure are already well known. But the hydration and deterioration of cement materials are inherently multiscale processes with more complex compositional, thermodynamic, and atomic structure changes that so far have defied most attempts at rigorous microstructure modelling. Therefore, microstructure models of cementitious materials have developed along a different path that is forced

to neglect many of these complexities that are incompletely understood. Such simplifications limit the applicability of such models and require extensive comparisons to gain confidence in their results. This article discusses how microstructural models attempt to capture the key details of microstructural development and how the information can be usefully applied towards the development of cement science.

2 Why microstructure development is important

The type and arrangement of solids, liquids and voids in the microstructure influence the engineering properties of cement paste. As a simple example, linear elastic moduli of the cementitious matrix are known to depend on the volumes of the phases including the pores, their sizes, their arrangement and their individual mechanical properties [7,8]. Transport properties also depend on the size and volume of pores, their connectivity, and the properties of the pore walls [9,10]. Not just the capillary pores, but also the nanoscale pores within the hydration products and the interfaces between hydration products contribute to the transport properties of cementitious pastes. Shrinkage, cracking and durability are also influenced both by the characteristics of the pores, the physical and chemical properties of the solids and the pore-solution. While initial numerical models of concrete assumed uniform paste properties, e.g., [11], the complex process of microstructural development in cement paste was soon seen to be important to model, e.g., [12] (Figure 1).

* Corresponding author: Shashank Bishnoi, E-mail: bishnoi@iitd.ac.in

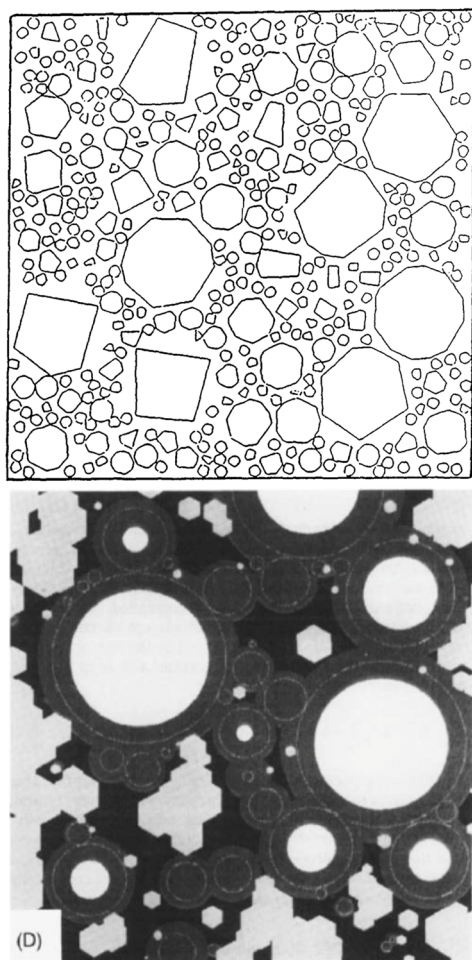


Figure 1. Simulated meso-structure of a concrete from Sadouki 1987 [11] showing spherical aggregates in a matrix of mortar (top) and simulated microstructure of a cement paste showing hydration products depositing over spherical cement particles and in the pores from Jennings and Johnson [12] (reproduced with permission) (bottom).

Cement microstructure evolves by hydration, creep, shrinkage, drying, deterioration and other processes throughout its lifetime. The ability to accurately simulate all such processes would be a powerful tool to replicate and study the structure-property relationships as the material interacts with its environment. However, most currently available microstructure models are limited to simulating hydration and its associated microstructural development [13-15]. Hydration of cementitious materials happens by a large number of coupled multi-step reaction processes mediated by a common pore solution. Each of these processes involves at least three essential steps of dissolution, diffusion and precipitation [16]. As the reactants dissolve, they dissociate into ionic species and change the pore solution's composition. While some of the reactants dissolve relatively rapidly, the dissolution of others may be inhibited by internal or external factors such as bond strength, structural defects, or solution concentrations. For example, the rate of dissolution of dicalcium silicate (or belite) may be lower when combined with tricalcium silicate (alite) than it is by itself because the more rapid alite dissolution increases the

saturation with respect to belite [17,18]. Precipitation of a hydration product takes place when the activities of ions in the solution exceed the equilibrium solubility of that phase. While most hydration products are less soluble than the unhydrated cementitious phases, they also have finite solubility and therefore exert an influence on the pore solution composition [19].

The phases that precipitate and their morphology depend on the availability of other dissolved ions and any space constraints in the microstructure [20-24]. Precipitation must lower the Gibbs energy of the system, but any number of different precipitation products can often lower the Gibbs energy. The specific product assemblage that forms is determined from among the thermodynamically allowed ones by kinetic factors [19,25]. The locations where the phases precipitate also depend on the relative concentration of the ions. Although the solution concentrations are fairly homogeneous, gradients that drive diffusion and influence dissolution rates are often significant especially at early ages. Some of the hydration products, such as calcium silicate hydrate (C-S-H), are observed to preferentially precipitate on or near the surface of the cement particles, but other products, such as calcium hydroxide (CH, conventional cement chemistry notation is used where convenient, with C = CaO, S = SiO₂, H = H₂O, etc.), appear to precipitate away from the cement particles [23,26,27]. The differences in location of the phases could have both thermodynamic and kinetic origins, however. One plausible explanation is that the supersaturation of the solution with respect to C-S-H could rapidly rise near the cement surfaces due to an accumulation of relatively less mobile silicate ions there, promoting an early nucleation of C-S-H on or near those surfaces. The solution does not reach supersaturation with respect to CH until considerably later [27], and the Ca²⁺ and OH⁻ ions involved in its precipitation are relatively more mobile [21,28].

The development of microstructure caused by hydration reactions can itself influence the rates of subsequent hydration reactions. Factors such as the mobility of ions and water through the microstructure, the accessibility of surfaces where dissolution and precipitation can take place and the availability of space for growth of products influence not just the rate at which hydration progresses, but also the properties of the hydration products. The water-filled pore space that serves as the highway for transport of ions decreases dramatically in size and volume and becomes more tortuous as the microstructure develops [29-31]. At the same time, some of this pore space can lose its water as a result of chemical shrinkage or drying [32].

Given the complex interactions among various elements in the microstructure, modelling was foreseen to play an important role in reconciling the influences of various phases and scales, beginning with the work of Pommersheim [33] and especially Jennings [34]. Several models and modelling approaches have been developed over the years that predict, with varying levels of success, the performance of cementitious materials and help understand the development of the microstructure itself [35]. However, the foregoing discussion in this section shows why the complexity

and the limited understanding of the processes make it difficult to create accurate models. This article discusses the key inputs, opportunities, and challenges involved in modelling the microstructure of cement paste.

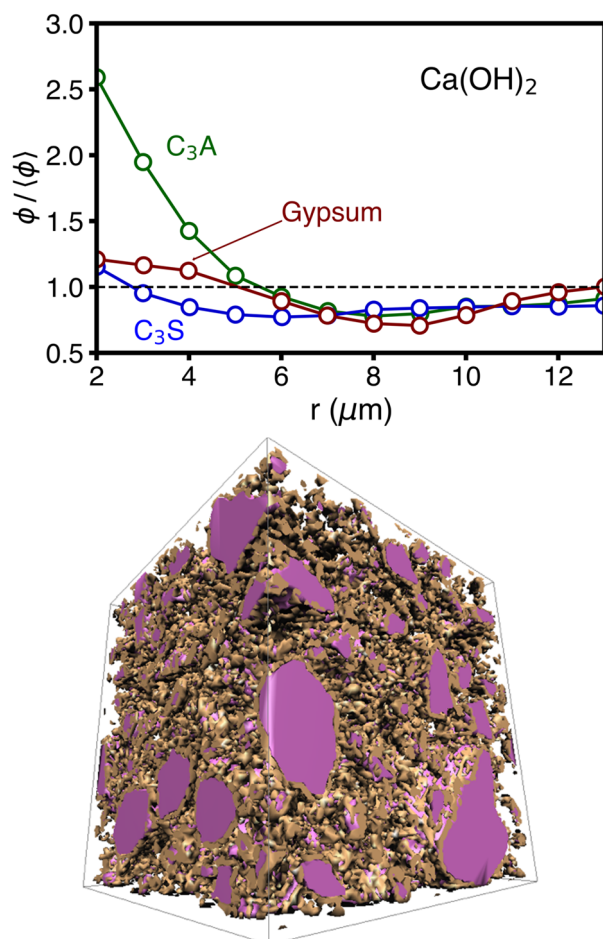


Figure 2. Radial distribution of concentration of CH normalised to its average concentration from the surface of various phases (top); kinetic cellular automaton simulation of the precipitation of CH in solution demonstrating the influence of non-uniform concentrations (bottom). The algorithm details and assumptions of the model producing these simulation results are provided fully in Ref. [28].

3 Microstructural modelling

Microstructural models attempt to recreate a digital replica of the important features of the microstructure of cementitious materials. However, both computational limitations and our incomplete understanding of the underlying chemistry make it unfeasible to represent the microstructure in every particular. Instead, models generally focus on specific properties, from setting time to elastic moduli to durability indices, that are more relevant to their objectives. Different approaches can be formulated to capture various important properties of the microstructure. For example, a two-dimensional slice from 3D numerical microstructure generated using CEMHYD3D [14] is compared to one generated by μic [15] in Figure 3. Briefly, CEMHYD3D uses a digital-image, agent based approach to simulate diffusion and reactions in these systems by random walkers and a catalog

of user-defined stochastic reaction rules, respectively. In contrast, μic is a vector based model that uses deterministic equations to predict the microstructure development. A detailed review of these and other popular methods of modelling hydration and/or microstructure, as well as their limitations can be found elsewhere [35]. The remainder of this section describes how microstructure modelling can help understand and predict just a few of the many important properties of cement pastes and highlights the key challenges to be expected when doing so.

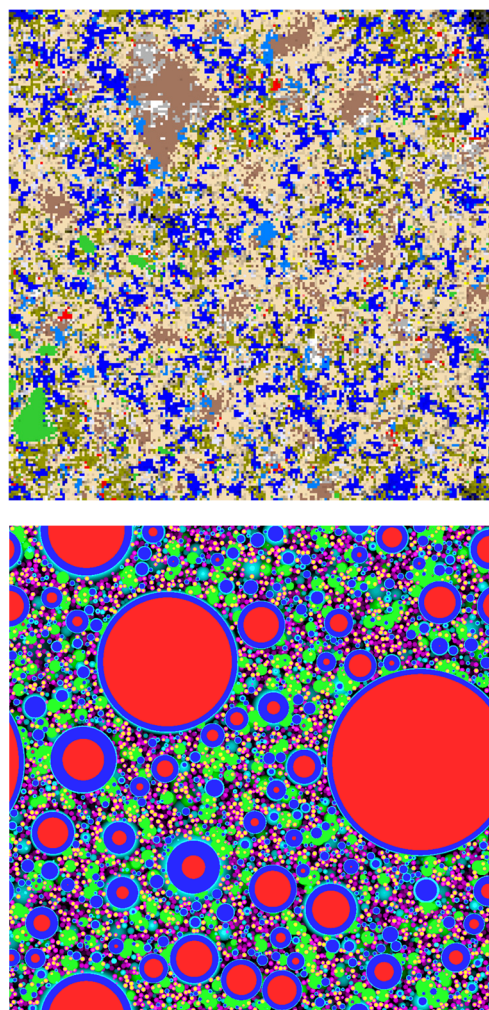


Figure 3. Slices of $100\mu\text{m}$ size from three-dimensional microstructures of hydrated cement pastes simulated using CEMHYD3D showing a microstructure after 72 hours of hydration of a Portland cement with $w/s = 0.45$ and a 5 wt% replacement by limestone (bright green) (top) and μic showing a microstructure after 72 hours of hydration of a cement paste with $w/s = 0.40$ and 15% replaced by inert filler (yellow) (bottom).

4 Rheology

Modelling cement paste rheological properties could provide a better understanding of the flow and workability of concrete. More importantly, it could help guide the design of mixtures and additives that are optimized for a specific application. However, there have been few applications of microstructure models to the rheological properties of

cement pastes. While rheology is known to be influenced by the volume fraction of solids, particle morphology and surface characteristics, the forces between the particles and the characteristics of the liquid [36-38], most of these are difficult to capture in microstructural models. Most models involve assumptions regarding the shapes and distribution of particles, and the results are consequently dependent on these assumptions. Furthermore, limited knowledge on inter-particle forces makes it difficult to model the dynamics of the movement of these particles in water. Despite these challenges, significant strides have been made in high-performance microstructure models of suspension rheological properties that are applicable to cement paste [39-41]. An example of a simulation of the flow of a suspension of cubical shaped particles can be seen in Figure 4. It is felt that in the future, such models can be useful in understanding phenomena such as thixotropy, shear thinning, shear thickening, etc. and also in the design of chemical admixtures for blended cements.

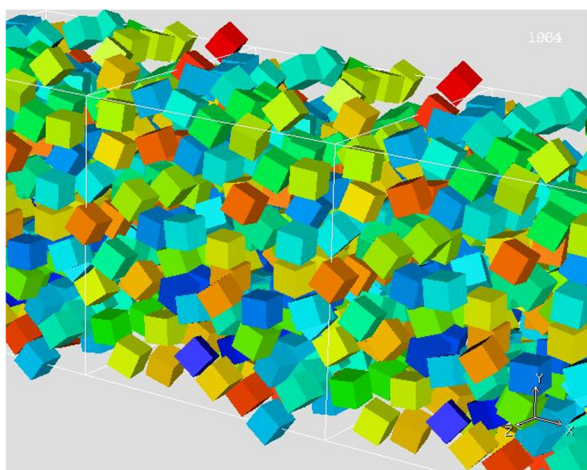


Figure 4. Simulation of the flow of a suspension of cubical particles [Nicos Martys, personal communication]

5 Hydration

Hydration is the process of the reaction of water with the unhydrated cement phases to produce solid hydrates. Cement is a complex mixture of several reactive phases, and the hydration reactions are typically simplified, sometimes greatly so, in microstructure models. Dissolution of the reactive phases into the pore solution happens simultaneously but at different rates, and this sets up a complex system of diffusing and reacting species in a common medium. The concentrations in this solution influence the driving force for, and rates of, both dissolution and precipitation of solid hydration products. Variability in initial phase proportions in different cements, and the impurities within them, can cause significant variability in the pore solution, especially at early times. This solution variability causes variations in the composition, morphology, and properties of hydration products, especially C-S-H but also the AFt and AFm phases [22,42-44]. The calcium to silicon molar ratio, substitution with metals, gel porosity and morphology of C-S-H are all known to depend sensitively on

the type and concentration of dissolved ions, the availability of water, and temperature. Similarly, the morphology and distribution of other hydration products such as CH are influenced by similar factors. In addition, adsorption and formation of surface altered layers may radically affect the rate and course of microstructure development despite the fact that they are difficult to observe and remain poorly quantified [45-48].

This state of affairs makes the accurate microstructure modelling of hydration quite problematic. Models have been developed that can accommodate these complexities in multiphase systems if given sufficient input, and could therefore accurately simulate the individual processes of dissolution, diffusion and precipitation. However, the required input data include intrinsic rate constants, nucleation energy barriers, comprehensive thermodynamic data on all possible phases, adsorption isotherms and the conditions of formation of surface altered layers. As already stated, most of these data are not available even for relatively simple cement-based systems such as Portland cement. Moreover, even when provided the appropriate input data these simulations are computationally intensive.

While other approaches to model hydration rely on empirical information on the quantities, characteristics and distribution of hydration products, in order to model any system using these approaches, a large amount of information regarding the rates of dissolution, the quantities of products, the stoichiometry and kinetics of reactions and the spatial distribution of their products would be required for that system. Therefore, despite being more computationally efficient, these approaches are less versatile and less suitable for prediction of properties have not been already measured experimentally. The simulation of hydration is also affected by the limitations of the approaches, which have been discussed elsewhere [35].

6 Setting time

Although setting is often considered to be a continuous process rather than a discrete event, it can be considered to be the time at which the first connected chain of solids forms that can transfer forces through the material. Microstructure models can be queried to detect the onset of hardening, either by searching the structure for a rigidity percolation threshold [49,50] or by computing the microstructure's shear modulus using a linear elastic finite element calculation [8]. Therefore, the problem comes down again to how accurately a given model predicts the microstructural state as a function of time. Besides the challenges of accurately simulating the dissolution and precipitation processes described previously, factors such as the initial distributions in cement particle size and shape, degree of agglomeration among cement particles must be considered for predicting time of set. Particle size distribution is commonly measured, while shape distribution and agglomeration are more challenging but still possible [51].

7 Mechanical properties

Microstructural models have been widely used to study the development of the mechanical properties of hydrating cement pastes, mortars, or concrete. While most of the work has been limited to modelling of the paste as a linear elastic solid [8,52,53], some work on the non-linear behavior, brittle fracture [54-57], and viscoelastic/viscoplastic properties of the paste [58-62] is also available. Two main approaches, analytical and numerical, have been used to homogenise the properties of cement paste for these purposes. While the analytical approaches are generally computationally more efficient, they neglect the arrangement of phases in the microstructure and only use limited information available in microstructural models [63,64]. The computational expense of using microstructural models is, therefore, often not justified for the application to analytical homogenisation. In contrast, numerical homogenisation approaches such as the finite element method (FEM) are able to utilise much more information available in microstructural models, but they involve a large number of simplifications and assumptions. For example, due to the high computational costs of FEM, numerical microstructures are often simplified before they are meshed. The process of meshing itself leads to artefacts, such as artificial connections between elements and ignoring of small elements, that directly influence the mechanical properties being modelled [65]. This is especially true during the early ages of hydration. Another major barrier to the modelling of the elastic properties of paste is the limited availability of data of the mechanical properties of the individual unhydrated and hydrated cement phases. While some values of elastic moduli of these phases are available in the literature, a large variation from one work to another, and even within the same work can be found [8,66-68]. Still, it has been seen that the elastic properties of cement paste can be modelled quite accurately [8,53,64], especially during later ages of hydration (Figure 5).

While compressive strength is arguably the most important mechanical property of a cement paste, very little success has been gained through its modelling. One of the reasons for this is the manner in which compressive strength is defined. While the term compressive strength implies that it measures the stress at which a material would fail under compression, actual laboratory tests produce cracks due to tension in the direction perpendicular to the applied compression which lead to the failure of specimens. Given the limited understanding of the tensile strength of concrete and the factors that influence it, the process of failure becomes difficult to simulate. While fracture mechanics could be used to simulate the process of cracking in cement pastes [55,57], it would require the availability of parameters, such as the surface energy of cracks, which are difficult to measure. Additionally, the brittle behaviour of pastes makes following the crack paths difficult.

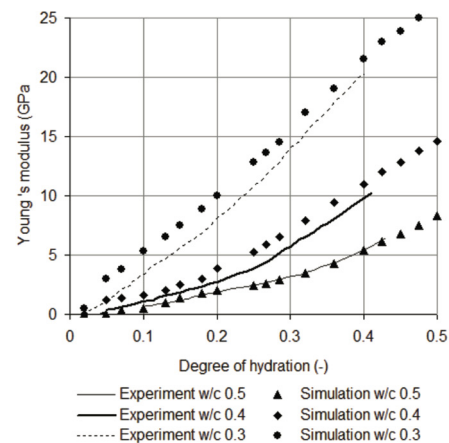
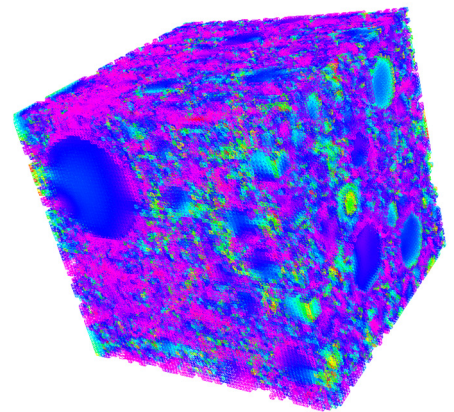


Figure 5. The distribution of strain on a cement microstructure upon the application of a uniform stress [Cyrille Dunant, personal communication] (top) and a comparison of simulated elastic modulus of cement pastes with experimentally measured values at various water to cement ratios [69] (bottom).

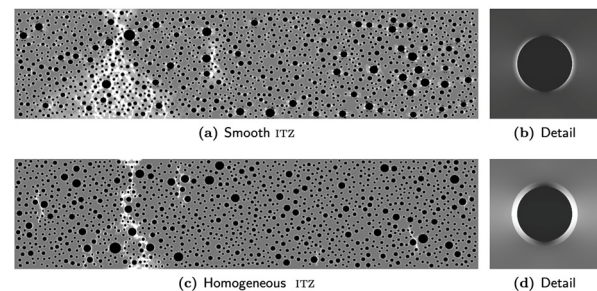


Figure 6. Simulation of influence of properties of interfacial transition zone on crack propagation in concrete using extended finite elements; assuming a smooth transition of properties in the ITZ (top) and a uniform properties in the ITZ (bottom) [57].

Creep and shrinkage are important properties that can potentially be simulated using microstructural models. While some work on these models is available in the literature [58-62], most of these models have been used to explore the consequences of different proposed mechanisms and typically require substantial calibration to reproduce experimental results. Despite the significantly improved understanding of the mechanisms underlying creep and shrinkage, the processes themselves are difficult to model. Both processes are greatly influenced by the characteristics of

the pore-network and the mechanical properties of the solids. Additionally, due to the limited information available about the behaviour of the individual phases, results obtained from such models rarely agree with experimental results.

8 Transport properties

The pore structure of cement binder is the most influential factor in determining the transport properties of concrete, so properties like the formation factor and permeability are, in principle, ideal candidates for microstructure modelling. Despite this, results have shown that the properties obtained through models can differ widely from those observed experimentally [70,71]. While a part of this observation can be attributed to the indirect ways by which the pore-characteristics are measured experimentally, a large part of the difference arises due to our limited understanding of the hydration products, their distribution and the flow of fluids through them. For example, while most models simulate flow through capillary pores, it has been shown that the flow through the gel pores of C-S-H makes an important contribution, and that the porosity in cement paste spans a continuous size distribution without clear demarcations that would otherwise make homogenization a clear-cut exercise [72]. Although models that simulate diffusion or hydrodynamic flow through hydration products are available [73], they often require significant simplifications to the microstructures before these simulations can be carried out.

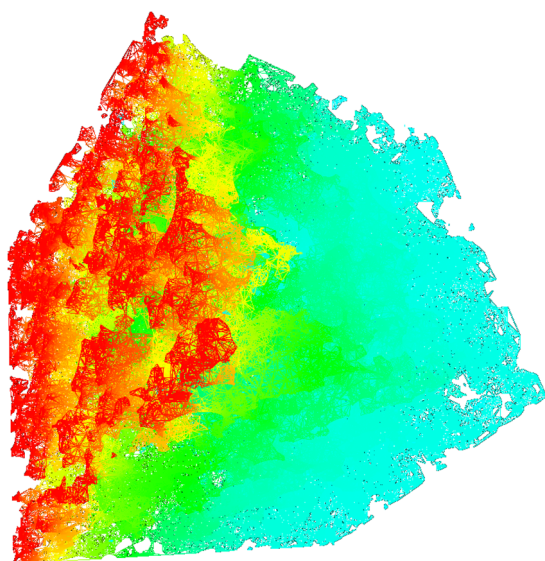


Figure 7. Simulation of diffusion of species through hydration products in a cement paste with unhydrated cement being impermeable. [Cyrille Dunant, personal communication]

It is envisaged that in the future, methods will be developed to model the flow of fluids and ions and the coupled reactions that occur at the same time as these transport processes. This would allow the modelling of chemical and physical evolution processes, such as deterioration and healing, in the microstructure.

9 The way to go

This paper has tried to indicate that microstructural models have the potential to improve the prediction of the properties of cement pastes, but that the results from those efforts so far have been limited by simplifications that are forced upon the models because of gaps in fundamental data and in our understanding of the basic underlying physicochemical processes. These limitations do not imply that these models are currently of no use, only that users must always be aware of the underlying limitations of the models and the influence that they have on the results. Since it will be difficult to develop models that address all the important aspects of microstructural development that are likely relevant to all the properties that we may be interested in, development of different approaches along parallel tracks to target specific properties is likely to be a more fruitful approach. Keeping these methods consistent with each other, and designing models of different properties to communicate with each other, will be important for the simulation of properties, such as creep, that may depend on several models. Finally, while most experimental work today focusses on obtaining empirical information regarding specific systems, experimental programmes that target the understanding of parameters and processes that can be simulated in these models will be required.

Authorship statement (CRediT)

Shashank Bishnoi: Conceptualization; Investigation; Resources; Data Curation; Writing – original draft; Writing – review and editing; Visualization

Jeffrey W. Bullard: Conceptualization; Investigation; Resources; Data Curation; Writing – original draft; Writing – review and editing; Visualization

References

- [1] W.J. Boettinger, J.A. Warren, C. Beckermann, A. Karma, Phase field simulation of solidification, *Annu Rev Mater Res*, 32 (2002) 163-194. <https://doi.org/10.1146/annurev.matsci.32.101901.155803>
- [2] L. Gránásy, T. Pusztai, G. Tegze, J.A. Warren, J.F. Douglas, Growth and form of spherulites, *Phys Rev E* 72 (2006) 011605. <https://doi.org/10.1103/PhysRevE.72.011605>
- [3] I. Steinbach, Phase-field models in materials science, *Model Simul Mater Sci Eng* 17 (2009) 073001. <https://doi.org/10.1088/0965-0393/17/7/073001>
- [4] V. Tikare, E.A. Holm, Application of the Potts model to simulation of Ostwald ripening, *J Am Ceram Soc* 81 (1998) 485-491. <https://doi.org/10.1111/j.1151-2916.1998.tb02366.x>
- [5] V. Tikare, E.A. Holm, D. Fan, L.-Q. Chen, Comparison of phase-field and Potts models for coarsening processes, *Acta Materialia* 47 (1999) 363-371. [https://doi.org/10.1016/S1359-6454\(98\)00313-9](https://doi.org/10.1016/S1359-6454(98)00313-9)
- [6] M. Braginsky, V. Tikare, E. Olevsky, Numerical simulation of solid state sintering, *Int J Solids Struct* 42 (2005) 621-636. <https://doi.org/10.1016/j.ijsolstr.2004.06.022>
- [7] G. Constantinides, F.-J. Ulm, The effect of two types of C-S-H on the elasticity of cement-based materials, results from nanoindentation and micromechanical modelling, *Cem Concr Res* 34 (2004) 67-80. [https://doi.org/10.1016/S0008-8846\(03\)00230-8](https://doi.org/10.1016/S0008-8846(03)00230-8)
- [8] C.J. Haecker, E.J. Garboczi, J.W. Bullard, R.B. Bohn, Z. Sun, S. Shah, T. Voigt, Modeling the linear elastic properties of Portland cement paste, *Cem Concr Res* 35 (2005) 1948-1960. <https://doi.org/10.1016/j.cemconres.2005.05.001>
- [9] J. Bear, *Dynamics of Fluids in Porous Media*, Elsevier, New York, 1972.

- [10] J. Marchand, D.P. Bentz, E. Samson, Y. Maltais, Influence of calcium hydroxide dissolution on the transport properties of hydrated cement systems. In: *Materials Science of Concrete: Calcium Hydroxide in Concrete*, 113-129, American Ceramic Society, Westerville, OH, 2001.
- [11] H. Sadouki, Simulation et analyse numerique du comportement mecanique de structures composites, PhD Thesis, Ecole Polytechnique Fédérale de Lausanne (1987).
- [12] H.M. Jennings and S.K. Johnson, Simulation of microstructure development during the hydration of a cement compound, *J Am Ceram Soc*, 69 (1986) 790-795. <https://doi.org/10.1111/j.1151-2916.1986.tb07361.x>
- [13] K. van Breugel, Models for prediction of microstructural development in cement-based materials. pp. 91-106 in *The Modelling of Microstructure and Its Potential for Studying Transport Properties and Durability*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996. https://doi.org/10.1007/978-94-015-8646-7_4
- [14] D.P. Bentz, Three-dimensional computer simulation of cement hydration and microstructure development, *J Am Ceram Soc* 80 (1997) 3-21. <https://doi.org/10.1111/j.1151-2916.1997.tb02785.x>
- [15] S. Bishnoi, K.L. Scrivener, μ c: A new platform for modelling the hydration of cements, *Cem Concr Res* 39 (2009) 266-274. <https://doi.org/10.1016/j.cemconres.2008.12.002>
- [16] J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, K.L. Scrivener, J.J. Thomas, Mechanisms of cement hydration, *Cem Concr Res* 41 (2011) 1208-1223. <https://doi.org/10.1016/j.cemconres.2010.09.011>
- [17] S. Garrault, A. Nonat, Hydrated layer formation on tricalcium and dicalcium silicate surfaces: experimental study and numerical simulations, *Langmuir* 17 (2001) 8131-8138. <https://doi.org/10.1021/la011201z>
- [18] L. Nicoleau, A. Nonat, D. Perrey, The di- and tricalcium silicate dissolutions, *Cem Concr Res* 47 (2013) 14-30. <https://doi.org/10.1016/j.cemconres.2013.01.017>
- [19] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of portland cement, *Cem Concr Res* 36 (2006) 209-226. <https://doi.org/10.1016/j.cemconres.2005.03.001>
- [20] H.M. Jennings, B.J. Dalgleish, P.L. Pratt, Morphological development of hydrating tricalcium silicate as examined by electron microscopy techniques, *J Am Ceram Soc* 64 (1981) 567-572. <https://doi.org/10.1111/j.1151-2916.1981.tb10219.x>
- [21] H.F.W. Taylor, *Cement Chemistry*. 2nd Edition. Thomas Telford, London 1997. <https://doi.org/10.1680/cc.25929>
- [22] I.G. Richardson, Tobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C-S-H: applicability to hardened pastes of tricalcium silicate, β -dicalcium silicate, Portland cement, and blends of portland cement with blast-furnace slag, metakaolin, or silica fume, *Cem Concr Res* 34 (2004) 1733-1777. <https://doi.org/10.1016/j.cemconres.2004.05.034>
- [23] E. Gallucci, K. Scrivener, Crystallisation of calcium hydroxide in early age model and ordinary cementitious systems, *Cem Concr Res* 37(2007) 492-501. <https://doi.org/10.1016/j.cemconres.2007.01.001>
- [24] A.V. Girão, I.G. Richardson, R. Taylor, R.M.D. Brydson, Composition, morphology and nanostructure of C-S-H in 70% white Portland cement-30% fly ash blends hydrated at 55 °C, *Cem Concr Res* 40 (2010) 1350-1359. <https://doi.org/10.1016/j.cemconres.2010.03.012>
- [25] P.W. Brown, Phase equilibria and cement hydration. pp. 73-93 in *Materials Science of Concrete*, Volume 1. J. Skalny, Ed. American Ceramic Society, Westerville, OH 1989.
- [26] S. Garrault, E. Finot, E. Lesniewska, A. Nonat, Observation directe de la croissance d'hydrosilicate de calcium sur des surfaces d'alite et de silice par microscopie à force atomique, *Comptes Rendus de l'Academie de Sciences - Serie IIa: Sciences de la Terre et des Planetes* 327(1998) 231-236. [https://doi.org/10.1016/S1251-8050\(98\)80057-8](https://doi.org/10.1016/S1251-8050(98)80057-8)
- [27] J.W. Bullard, R.J. Flatt, New Insights Into the Effect of Calcium Hydroxide Precipitation on the Kinetics of Tricalcium Silicate Hydration, *J Am Ceram Soc* 93 (2010) 1894-1903. <https://doi.org/10.1111/j.1151-2916.2010.03656.x>
- [28] J.W. Bullard, E. Enjolras, W.L. George, S.G. Satterfield, J.E. Terrill, A parallel reaction-transport model applied to cement hydration and microstructure development, *Modelling and simulation in material science and engineering*, 18 (2010) 16. <https://doi.org/10.1088/0965-0393/18/2/025007>
- [29] H. Cheng-yi, R.F. Feldman, Influence of silica fume on the microstructural development in cement mortars, *Cem Concr Res* 15 (1985) 265-294. [https://doi.org/10.1016/0008-8846\(85\)90040-7](https://doi.org/10.1016/0008-8846(85)90040-7)
- [30] D.N. Winslow, M. Cohen, D.P. Bentz, K.A. Snyder, E.J. Garboczi, Percolation and pore structure in mortars and concrete, *Cem Concr Res* 24 (1994) 25-37. [https://doi.org/10.1016/0008-8846\(94\)90079-5](https://doi.org/10.1016/0008-8846(94)90079-5)
- [31] G. Ye, K. van Breugel, A. Fraaij, Experimental study and numerical simulation on the formation of microstructure in cementitious material at early age, *Cem Concr Res* 33 (2003) 233-239. [https://doi.org/10.1016/S0008-8846\(02\)00891-8](https://doi.org/10.1016/S0008-8846(02)00891-8)
- [32] T.C. Powers, Absorption of water by Portland cement paste during the hardening process, *Ind Eng Chem* 27 (1935) 790-794. <https://doi.org/10.1021/ie50307a011>
- [33] J. Pommersheim, J.R. Clifton, Mathematical modeling of tricalcium silicate hydration, *Cem Concr Res* 9 (1979) 765-770. [https://doi.org/10.1016/0008-8846\(79\)90072-3](https://doi.org/10.1016/0008-8846(79)90072-3)
- [34] H.M. Jennings, S.K. Johnson, Simulation of microstructure development during the hydration of a cement compound, *J Am Ceram Soc* 69 (1986) 790-795. <https://doi.org/10.1111/j.1151-2916.1986.tb07361.x>
- [35] J.J. Thomas, J.J. Biernacki, J.W. Bullard, S. Bishnoi, J.S. Dolado, G.W. Scherer, A. Lüttge, Modeling and simulation of cement hydration kinetics and microstructure development, *Cem Concr Res* 41 (2011) 1257-1278. <https://doi.org/10.1016/j.cemconres.2010.10.004>
- [36] L. Nachbaur, P.-C. Nkinamubanzi, A. Nonat, J.-C. Mutin, Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration, *Jo Colloid Interface Sci* 202 (1998) 261-268. <https://doi.org/10.1006/jcis.1998.5445>
- [37] L. Nachbaur, J.C. Mutin, A. Nonat, L. Choplin, Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting, *Cem Concr Res* 31 (2001) 183-192. [https://doi.org/10.1016/S0008-8846\(00\)00464-6](https://doi.org/10.1016/S0008-8846(00)00464-6)
- [38] C. Labbez, I. Pochard, B. Jönsson, A. Nonat, C-S-H/solution interface: experimental and Monte Carlo studies, *Cem Concr Res* 41 (2011) 161-168. <https://doi.org/10.1016/j.cemconres.2010.10.002>
- [39] R.J. Flatt, N.S. Martys, L. Bergstrom, The rheology of cementitious materials, *Mater Res Bull* 29 (2004) 314-318. <https://doi.org/10.1557/mrs2004.96>
- [40] S.T. Erdogan, N.S. Martys, C.F. Ferraris, D.W. Fowler, Influence of the shape and roughness of inclusions on the rheological properties of a cementitious suspension, *Cem Concr Compos*, 30 (2008) 393-402. <https://doi.org/10.1016/j.cemconcomp.2008.01.003>
- [41] N.S. Martys, D. Lootens, W. George, P. Hébraud, Contact and stress anisotropies in start-up flow of colloidal suspensions, *Phys Rev E* 80 (2009) 031401. <https://doi.org/10.1103/PhysRevE.80.031401>
- [42] T. Matschei, B. Lothenbach, F.P. Glasser, The AFm phase in Portland cement, *Cem Concr Res* 37 (1007) 118-130. <https://doi.org/10.1016/j.cemconres.2006.10.010>
- [43] D.A. Kulik, Improving the structural consistency of C-S-H solid solution thermodynamic models, *Cem Concr Res* 41 (2011) 477-495. <https://doi.org/10.1016/j.cemconres.2011.01.012>
- [44] E. L'Hôpital, B. Lothenbach, K. Scrivener, D.A. Kulik, Alkali uptake in calcium alumina silicate hydrate (C-A-S-H), *Cem Concr Res* 85 (2016) 122-136. <https://doi.org/10.1016/j.cemconres.2016.03.009>
- [45] R.A. Livingston, J.S. Schweitzer, C. Rolfs, H.-W. Becker, S. Kubsky, Characterization of the induction period in tricalcium silicate hydration by nuclear resonance reaction analysis, *J Mater Res* 16 (2001) 687-693. <https://doi.org/10.1557/JMR.2001.0108>
- [46] F. Bellmann, D. Damidot, B. Möser, J. Skibsted, Improved evidence for the existence of an intermediate phase during hydration of tricalcium silicate, *Cem Concr Res* 40 (2010) 875-884. <https://doi.org/10.1016/j.cemconres.2010.02.007>
- [47] F. Bellmann, T. Sowoidnich, H.-M. Ludwig, D. Damidot, Analysis of the surface of tricalcium silicate during the induction period by x-ray photoelectron spectroscopy, *Cem Concr Res* 42 (2012) 1189-1198. <https://doi.org/10.1016/j.cemconres.2012.05.011>
- [48] E. Pustovgar, R.P. Sangodkar, A. Andreev, M. Palacios, B. Chmelka, F.R. Flatt, J.-B. d'Espinose de Lacaillerie, Understanding silicate hydration from quantitative analyses of hydrating tricalcium silicates, *Nature Communications* 7 (2016) 10952. <https://doi.org/10.1038/ncomms10952>
- [49] D. Stauffer, A. Aharony. *Introduction to Percolation Theory*. 2nd Ed. Taylor and Francis, London, 1994.
- [50] G.W. Scherer, J. Zhang, J.A. Quintanilla, S. Torquato, Hydration and percolation at the setting point, *Cem Concr Res* 42 (2012) 665-672. <https://doi.org/10.1016/j.cemconres.2012.02.003>

- [51] J.W. Bullard, E.J. Garboczi, A model investigation of the influences of particle shape on Portland cement hydration, *Cem Concr Res* 36 (2006) 1007-1015. <https://doi.org/10.1016/j.cemconres.2006.01.003>
- [52] P. Feng, C. Miao, J.W. Bullard, A model of phase stability, microstructure, and properties during leaching of Portland cement binders, *Cem Concr Compos* 49 (2014) 9-19. <https://doi.org/10.1016/j.cemconcomp.2014.01.006>
- [53] C.F. Dunant, J. Granja, A. Muller, M. Azenha, K.L. Scrivener, Microstructural simulation and measurement of elastic modulus evolution of hydrating cement pastes, *Cem Concr Res* 130 (2020) 106007. <https://doi.org/10.1016/j.cemconres.2020.106007>
- [54] Z. Chang, H.Z. Zhang, E. Schlangen, B. Savija, Lattice fracture model for concrete fracture revisited: calibration and validation, *Applied Sciences-Basel* 10 (2020) 4822. <https://doi.org/10.3390/app10144822>
- [55] M. Nitka, J. Tejchman, Modelling of concrete behaviour in uniaxial compression and tension with DEM, *Granular Matter* 17 (2015) 145-164. <https://doi.org/10.1007/s10035-015-0546-4>
- [56] R.V. Sagar, B.R. Prasad, S. Nazreen, R. Singh, Modeling mode-I fracture process in concrete at meso-scale: computational aspects of lattice model and a comparison between results of two dimensional simulation and acoustic emission measurements, *Eng Fract Mech* 210 (2019) 257-258. <https://doi.org/10.1016/j.engfracmech.2018.05.044>
- [57] C. Dunant, Experimental and modelling study of the alkali-silica reaction in concrete, PhD Thesis, Ecole Polytechnique Fédérale de Lausanne, Switzerland (2009)
- [58] X. Li, Z.C. Grasley, E.J. Garboczi, J.W. Bullard, Modeling the apparent and intrinsic viscoelastic relaxation of hydrating cement paste, *Cem Concr Compos* 55 (2014) 322-330. <https://doi.org/10.1016/j.cemconcomp.2014.09.012>
- [59] Q-H. Do, S. Bishnoi, K.L. Scrivener, Microstructural Modelling of Early Age Creep in Hydrating Cement Paste, *ASCE J Eng Mech* 142(2016) 04016086. [https://doi.org/10.1061/\(ASCE\)EM.1943-7889.0001144](https://doi.org/10.1061/(ASCE)EM.1943-7889.0001144)
- [60] X. Li, Z.C. Grasley, J.W. Bullard, P. Feng, Creep and relaxation of cement paste caused by stress-induced dissolution of hydrating solid components, *J Am Ceram Soc* 101 (2018) 4237-4255. <https://doi.org/10.1111/jace.15587>
- [61] A.B. Giorla, C.F. Dunant, Microstructural effects in the simulation of creep of concrete, *Cem Concr Res* 105 (2018) 44-53. <https://doi.org/10.1016/j.cemconres.2017.12.001>
- [62] Q-H. Do, S. Bishnoi, K.L. Scrivener, Microstructural Modelling of Autogenous Shrinkage in Portland Cement Paste at Early Age, *Engineering Computations*, 37 (2020) 3171-3186. <https://doi.org/10.1108/EC-08-2019-0353>
- [63] S. Beniwal, M. Sharma, S. Bishnoi, Mechanical property evaluation of composites based on $n + 1$ phase model and Mori-Tanaka theory, *Journal of Engineering Mechanics* 145 (2019) 1-12. [https://doi.org/10.1061/\(ASCE\)EM.1943-7889.0001564](https://doi.org/10.1061/(ASCE)EM.1943-7889.0001564)
- [64] M. Sharma, S. Bishnoi, Influence of properties of interfacial transition zone on elastic modulus of concrete: evidence from micromechanical modelling, *Construction and Building Materials* 246 (2020) 118381. <https://doi.org/10.1016/j.conbuildmat.2020.118381>
- [65] E.J. Garboczi, D.P. Bentz, Effect of statistical fluctuation, finite size error, and digital resolution on the phase percolation and transport properties of the NIST cement hydration model, *Cem Concr Res* 31 (2001) 1501-1514. [https://doi.org/10.1016/S0008-8846\(01\)00593-2](https://doi.org/10.1016/S0008-8846(01)00593-2)
- [66] V. Swamy, L.S. Dubrovinsky, Thermodynamic data for the phases in the CaSiO_3 system, *Geochimica et Cosmochimica Acta* 61 (1997) 1181-1191. [https://doi.org/10.1016/S0016-7037\(96\)00403-6](https://doi.org/10.1016/S0016-7037(96)00403-6)
- [67] K. Velez, S. Maximilien, D. Damidot, G. Fantozzi, F. Sorrentino, Determination by nanoindentation of elastic modulus and hardness of pure constituents of Portland cement clinker, *Cem Concr Res* 31 (2001) 555-561. [https://doi.org/10.1016/S0008-8846\(00\)00505-6](https://doi.org/10.1016/S0008-8846(00)00505-6)
- [68] H. Manzano, J.S. Dolado, A. Ayuela, Elastic properties of the main species present in Portland cement pastes, *Acta Materialia* 57 (2009) 1666-1674. <https://doi.org/10.1016/j.actamat.2008.12.007>
- [69] Q-H Do, Modelling Properties of Cement Paste from Microstructure: Porosity, Mechanical Properties, Creep and Shrinkage, PhD Thesis, Ecole Polytechnique Fédérale de Lausanne, Switzerland (2013).
- [70] D.P. Bentz, N.S. Martys, A Stokes permeability solver for three-dimensional porous media, NISTIR 7416, National Institute of Standards and Technology, Gaithersburg, MD, 2007. Available at <https://www.nist.gov/services-resources/software/stokes-three-dimensional-permeability-solver>. <https://doi.org/10.6028/NIST.IR.7416>
- [71] Q-H. Do, S. Bishnoi, K.L. Scrivener, Numerical simulation of porosity in cements, *Transport in Porous Media*, 99 (2013), 101-117 <https://doi.org/10.1007/s11242-013-0176-4>
- [72] M. Zalzale, P.J. McDonald, K. Scrivener, A 3D lattice Boltzmann effective media study: Understanding the role of C-S-H and water saturation on the permeability of cement paste, *Model Simul Mater Sci Eng* 21 (2013) 08016. <https://doi.org/10.1088/0965-0393/21/8/085016>
- [73] D.P. Bentz, Influence of silica fume on diffusivity in cement-based materials. II. Multiscale modeling of concrete diffusivity, *Cem Concr Res* 30 (2000) 1121-1129. [https://doi.org/10.1016/S0008-8846\(00\)00263-5](https://doi.org/10.1016/S0008-8846(00)00263-5)