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From electrons to infrastructure: Engineering concrete from the bottom up

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ABSTRACT

An approach rooted in fundamental, mechanistic models of concrete materials offers the only viable path for handling the enormous number of variables that are being introduced as new materials are added to the design space, and as new properties are mandated for a sustainable infrastructure. These models must begin at the smallest length scales relevant for concrete properties; in some cases this is the scale of electron interactions among atoms and ions. But concrete has complex chemical and structural properties that are manifested at greater length and time scales, so atomic scale models must ultimately be integrated with new models that capture behavior at mesoscopic and macroscopic scales. We refer to this methodology as the "bottom-up" approach because it proceeds from the smallest length scales. We describe this kind of modeling approach, include some recent results, and suggest some principles for collaboratively integrating multi-scale models.

Contents

1. Introduction[1]

The world's most used man-made substance, portland cement concrete, is also one of the world's most complex substances. Current worldwide annual production of portland cement stands at 2.13 billion tonnes, enough to produce some 23 billion tonnes of concrete each year. Moreover, concrete is used everywhere, including environments with extreme conditions of temperature and pressure, and it is expected to perform well over long periods of time under these diverse service conditions. Unfortunately, the massive use of concrete has a significant impact on the environment: the production of each tonne of portland cement requires about 1.6 tonnes of raw materials, primarily quartz and limestone, and releases about 0.9 tonnes of CO_2 into the atmosphere, thus being responsible for probably 5% of the world's greenhouse gas emissions [1,2]. One of the key near-term challenges for the cement industry is to reduce the greenhouse gas emissions, energy consumption, and natural resources associated with cement production by developing innovative and sustainable cement-based material solutions.

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[1] A number of extensive reviews have been written since the last International Congress on the Chemistry of Cement (ICCC) that have covered broadly exciting developments in the field of cement science, and this paper is not in competition with these reviews. Recently an unusually concentrated effort has been initiated at the Massachusetts Institute of Technology (MIT), with the theme of "bottom-up" engineering analysis and design, starting at the electron, atomic and molecular scales. For years the National Institute of Standards and Technology (NIST) has also been developing a similar approach, but starting at the micrometer scale. This paper focuses on the expertise and laboratory environments of the authors.

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Currently, the most feasible way to meet this challenge is to partially replace portland cement with other materials, including materials from industrial waste streams (e.g. fly ash from coal combustion and blast furnace slag from steel production, and perhaps even dust from cement kilns) and filler materials such as limestone with relatively low reactivity. Introducing such materials, however, often changes the workability, setting time, hardened properties, and durability of concrete. To offset some of these undesirable changes, chemical admixtures are often added in increasing quantities to modify the early-age properties and bring them back to within acceptable ranges. Concrete is a relatively "forgiving" material, but even so, the increasing use of these supplementary materials increases the size of the concrete "design space" exponentially and can cause unexpected changes to performance and durability. Our current understanding of how new materials or processing conditions can influence important properties such as creep, drying shrinkage, and permeability is wholly inadequate. As a result, the most complex and important problem in concrete science, which is to predict the durability of concrete structures in a given environment and under a specific load, is still largely unsolved, especially with the push to incorporate more reactive industrial by-product materials and fillers into the binder. The corresponding inability to accurately predict or reliably prevent premature deformation (creep) and deterioration (both chemical and physical) represents a huge global expense in maintenance and replacement of concrete structures [3,4]. We must obtain a fuller understanding of the chemistry and structure of cementitious binders to be able to utilize these new materials to their best advantage and to have confidence in both their early-age behavior and their long-term performance and durability. A major objective of materials science is to exploit a deep understanding of structure and relate this understanding to properties so that one can manipulate materials for a given purpose or design entirely new materials. That strategy has been spectacularly successful in fields ranging from metallurgy [5] to medicine [6,7], and it can also be for concrete.

1.1. The elusive nature of C–S–H[2]

In general terms, concrete durability is controlled by the physical distribution of solids, pores, and surfaces across a range of length scales, as well as the chemical and thermodynamic properties of the liquid and solid phases. A critical missing link is an adequate understanding at the atomic, molecular, and nanostructure scales. Calcium silicate hydrate (C–S–H) is at the core of the problem. The glue that holds concrete together and has the greatest contribution to many of its properties, C–S–H is a non-crystalline hydrate of variable composition that easily incorporates impurities and contains water, some of which is chemically bound and some of which is structurally important but not chemically bound. It is an extraordinarily difficult material to study from the point of view of basic research. The challenges include (1) great difficulty in characterizing the nanostructure due to its delicate and nearly amorphous structure, (2) heterogeneity across six orders of magnitude in length scale, and (3) its sensitivity to both the chemistry of the reactive components of the starting cement and the environmental conditions, particularly temperature and humidity, during curing and service. For example, when examined in the vacuum of an electron microscope, C–S–H is not the same material that exists within structural concrete. In fact, only a very few analytical techniques do not alter the structure in one way or another. But without a quantitative understanding of the structure at the bottom level (defined here as the structure at the scale between individual atoms and about 100 nm), it is difficult to evaluate how the structure changes with time, load, drying, and chemical composition, and nearly impossible to relate structure directly to properties. The problem will only be exacerbated in the near future as the building industry moves toward more sustainable materials, the chemical formulations of which are quickly moving into areas for which there is no experience base. Consequently, increasingly urgent questions will arise about durability and the fate of impurities such as mercury and radionuclides.

1.2. How models can help

Structure–property–processing relationships must be defined in terms of the scale that controls the property of interest. For C–S–H it is widely accepted that the *nano*scale structure controls many engineering properties such as the elastic moduli, creep and drying shrinkage. Perhaps Powers [8] in the 1940s was the first to focus attention on the importance of the nanostructure in cement paste. His work sparked intense speculation and controversy over the nanostructure, and the ensuing quest to understand properties at these length scales has been the topic of numerous research papers and conferences (see a recent review in Ref. [9]). However, because of the extreme difficulty of probing the structure of C–S–H at the finest scales, even the best efforts to define the nanostructure have produced only qualitative "cartoons", such as those shown in Fig. 1, at least until recently. In contrast, the history of models of cement paste *micro*structure, where capillary porosity and the distribution of phases can be observed, begins in the mid-1980s [10] but developed much more rapidly [11–13] because of the advent of experimental characterization methods at those coarser length scales. We will have more to say about microstructure models later, but for now we emphasize that the most important missing pieces of the puzzle are the fundamental mechanistic relationships between the nanostructure and properties of cement paste, particularly C–S–H. These relationships can be discovered through sufficiently powerful computational techniques that enable a comprehensive set of models for the atomic structure, the nanostructure, and the micrometer-scale structure of cement based materials. Use of these models is already growing rapidly and has led to unprecedented progress in understanding the nanostructure, mechanical properties, and, to some extent, dynamic chemical interactions between cement phases and their aqueous environment [14–20].

More comprehensive understanding at the atomic and nanostructure scales is a critical step forward, but engineering more sustainable concrete will require knowledge of how nanostructure–processing–property relationships participate in determining the static and time-dependent engineering properties of macroscopic concrete. In addition to the nanoscale picture, concrete materials have important, complex chemical and physical characteristics at length scales (1 μm to more than 10 mm) that are too large to capture with nanoscale simulations. Therefore, an important step in future engineering design of concrete will be the scaling up of calculated properties at the nanometer scale to different kinds of higher scale computational models, some of which already exist [21,22] that can simulate the microstructural and macroscopic evolution of structure and calculate properties under realistic environmental conditions.

A "bottom-up" multiscale modeling approach, spanning the finest length scales to macroscopic elements, is not a new idea in materials science, but it is only now beginning to be seriously pursued for cementitious materials. The rest of this paper briefly describes some important progress that has been made in this direction, both at the atomic and nanostructure scales and at greater scales. We will also outline strategies for how models can be integrated across multiple length and time scales, an important but difficult task.

2. From atoms to infrastructure

It may not be immediately obvious why structures at the atomic, nanometer and micrometer levels are important to understanding

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[2] Conventional cement chemistry notation is used throughout the manuscript (i.e., $C = CaO$, $S = SiO_2$, and $H = H_2O$).

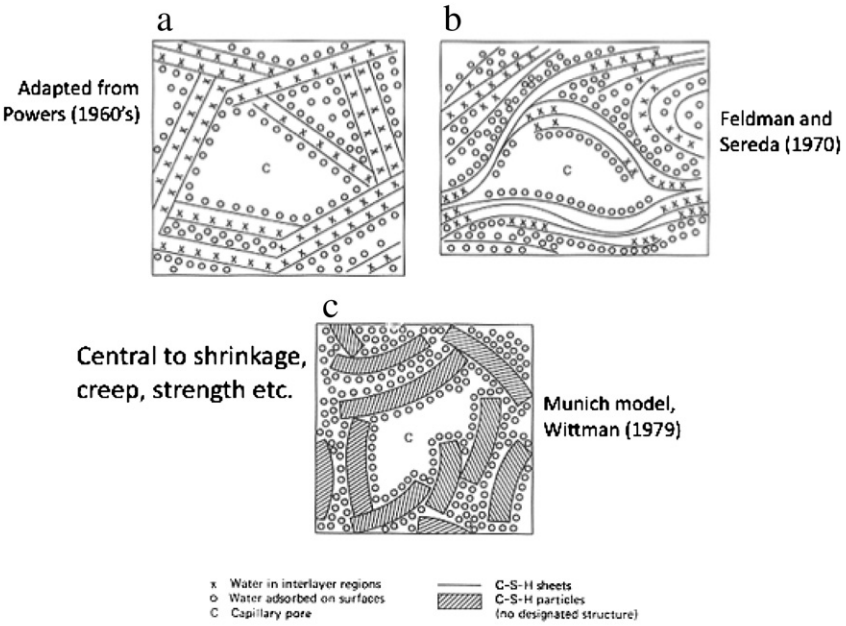

Fig. 1. Examples of schematic illustrations of the nanostructure of C–S–H appearing in text books. (a) Powers' model [8], (b) Feldman and Sereda's model [48], and (c) the Munich model [49]. Figure adapted from that originally appearing in Ref. [50].

engineering properties. It is worth providing a cursory overview of this subject to illustrate this fundamental aspect of materials science.

Though the cartoons in Fig. 1 are imprecise, they have furnished a broad understanding of the mechanisms that control many properties of cement; for example, that water in the smallest pores, the "gel porosity", plays a major role. Water exists within the solid in at least two states, that which is chemically bound and that which is mobile enough to evaporate when dried strongly. But neither the detailed structure of the solid nor the detailed physical chemistry of the water has been understood, especially under varied chemical compositions and physical conditions. This kind of understanding requires both equilibrium and kinetic considerations that are generally too complex to solve without comprehensive numerical models.

Perhaps the first statement that structure and property are related was Powers' use of the gel–space ratio,[3] X, to produce an expression for compressive strength, σ_c, of any concrete:

$$\sigma_c = AX^n, \tag{1}$$

where A and n are constants. While empirical, this expression was the first to capture the concept that porosity in fact controls strength, which is now a widely accepted concept for brittle materials. This concept is a powerful driving force behind the development of ultrahigh-strength cement based materials, where porosity is reduced to an absolute minimum by efficient packing of the cement grains in the original mix. The problem is that constants must be evaluated for each mix; they cannot be predicted from first principles. After years of research, enough is now known about the nanostructure to accurately predict the relative volumes of gel pores and capillary pores. The influence of variables such as temperature and relative humidity history is also better understood, but even in this simple case there are unknowns. The task ahead is to develop this level of understanding for materials in an increasingly large design space that includes new cement formulations.

This same problem exists for creep and drying shrinkage, properties that are immensely complicated by the influences of ambient history, the existence of reversible and irreversible components, and nonlinear coupling under both load and drying. Here again progress is providing fundamental information about the mechanisms behind deformation [23], which holds the potential of replacing empirical equations with scientifically grounded models.

The problem can be divided into two categories: 1) chemical kinetics and 2) structure at the small scale. Recent research has shown that the volume of gel pores is not constant in C–S–H [24]. Instead, C–S–H forms with at least two distinct morphologies, one with higher density and one with lower density. Furthermore, arguments have been presented that the structure is best described as variations of the packing of tiny particles, about 5 nm in diameter, that are connected with defined cohesion and friction [25]. This suggests that C–S–H is a granular material with bulk properties that depend on the chemistry, physical interactions, and packing density of the particles.

Closely related to the structure–property relationships is the question of the mechanisms that control the formation of nanostructure and microstructure. In other words, what controls the rates of the multiple coupled chemical reactions that characterize hydration? What controls the growth morphology of hydration products, and how does this relate to the setting of the material at early ages? These issues are controversial and have significant industrial implications. Various nucleation and growth models have been proposed (for a recent review see Ref. [26]), but without a detailed understanding of the structure these models remain unproven.

3. Relating nanostructure to properties and kinetics

Putting together the pieces of the nanostructure–property puzzle continues to be challenging, involving a synthesis of experimental techniques for observing or inferring nanostructure and strategies for building models. Success depends on defining representative volume elements at each length scale that can be experimentally probed but also can be linked to produce an upscaling approach for modeling, as shown in Fig. 2. With this approach, a general picture is now emerging. Among the important recent developments at the finest scales, ab initio calculations and molecular dynamic simulation methods have now produced a detailed picture, as shown in Fig. 3, of the precise composition and molecular structure of C–S–H, including the position and binding of water molecules in the interstitial porosity, that has been validated against numerous types

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[3] The gel–space ratio is the ratio of the volume of all hydration products, including any gel pores, to the volume of the hydration products plus capillary pores.

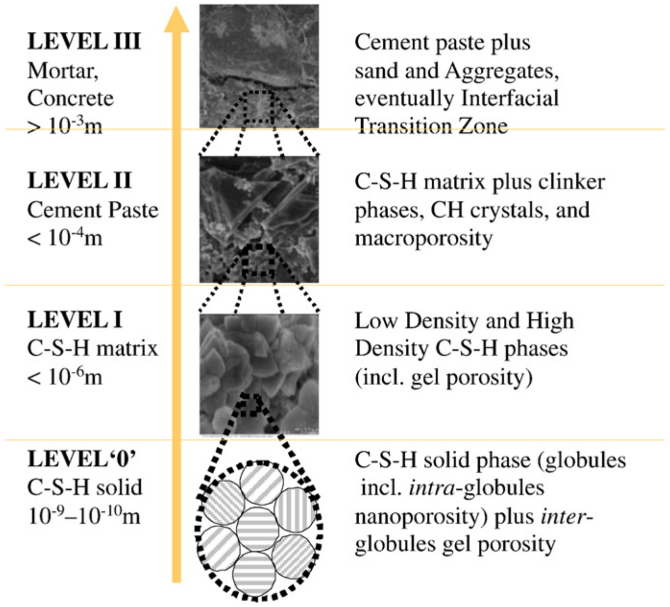

Fig. 2. Definition of representative volume elements for a multiscale modeling approach to concrete materials, showing the four primary scales and how they are linked. Figure adapted from that appearing in Ref. [51].

of experimental measurements [14,15]. These models are being developed at a rapid pace, and represent a huge step forward from the cartoons of the past. They can predict the changes in structure at different calcium contents, the location and binding energy of impurities, and the amount and location of water under various ambient conditions.

Significant progress also has been made at the next scale up, from 1 nm to 10 nm. Evidence of the granular nature of C–S–H is mounting and becoming increasingly accepted [16–20]. In fact, for C–S–H formed in neat portland cement pastes, the chemistry [17,18] and possible packing arrangements [16] of the grains have now been described in enough detail (see Fig. 4) to establish that they aggregate together into regions of different densities [19,20]. Again, these nanoscale models are convincing because they have reconciled a large number of experimental observations that previously seemed contradictory (see Ref. [16] for a fuller discussion).

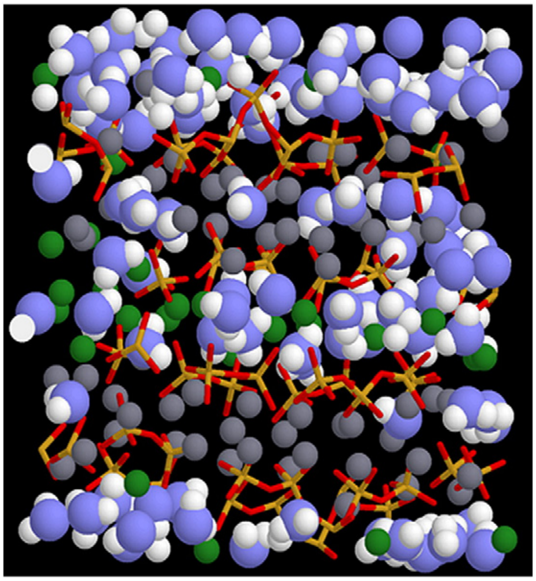

Fig. 3. Detailed molecular structure of C–S–H under realistic moisture conditions in neat portland cement paste, showing the positions and bonding environments of calcium, silicate tetrahedral, hydroxyl groups, and water [14]. Yellow and red lines represent Si–O bonds, green and gray spheres are calcium, and blue and white spheres are the oxygens and hydrogens of water molecules, respectively.

The structure and properties of C–S–H in neat portland cement pastes are now being anchored to an increasingly firm mechanistic foundation. Instead of the qualitative pictures like those in Fig. 1, at length scales up to 10 nm, models are now probing the exact position and binding energy of each atom in C–S–H, as well as its nanogranular composition, properties, and possible packing arrangements. This is remarkable progress in a relatively short span of time, and the same method of attack can be used to map out how the composition, structure, and properties of C–S–H are modified when the types and chemical potentials of molecules in the adjacent solution are changed by the introduction of other materials such as fly ash and slag.

3.1. Kinetics: dissolution of cement phases

How rapidly will a given concrete mix set? Why does the addition of some fly ash materials cause long delays in setting? What is the effect on properties and service life of prolonged exposure to elevated temperatures or high doses of radiation? These and related questions – important for engineering applications but of a different character than the structure–property relations addressed earlier – are concerned with the time-dependence of the structure at multiple length scales.

From several minutes after mixing until several hours thereafter, the rates of dissolution of cement minerals are quite low (although not zero unless the mix is intentionally retarded by admixtures) and the composition of the aqueous solution changes very slowly if at all. This solution composition, along with the energy barrier to nucleation of phases like C–S–H, portlandite, and ettringite controls the formation rate and location of nuclei of those phases at early ages. Surprisingly little is known quantitatively about these phenomena in cementitious systems, primarily because they involve continual changes in the surface topography and number of active dissolution sites, and because the growing phases are coupled by the fact that they all draw from a common pool of reactants. For this reason, molecular simulation techniques such as kinetic Monte Carlo methods are the tools of choice to help interpret observations of phases that may be present at crystal surfaces, as well as the number density of crystal surface dissolution sites, made with experimental techniques like atomic force microscopy (AFM) and vertical scanning interferometry (VSI) [27]. The ability to compare the evolution of a virtual crystal surface with the experimental result at molecular resolution is now ushering in advances in understanding and measurement of kinetic parameters involved in dissolution, nucleation, and growth [28]. A fuller discussion of recent techniques and results is available in Ref. [29], but the key is that this kind of cooperative experimental/simulation investigation is required to obtain quantitative information about rate parameters for individual dissolution, nucleation, and growth reactions. The same approach will continue to be applicable whether investigating the earliest stages of hydration or relatively slow degradation processes in mature concrete such as alkali–silica reactions or sulfate attack.

Comprehensive models of the nanoscale properties and kinetics will provide important benefits. Since they are based on first principles, they will be inherently extrapolative in the sense of being able to accommodate the influences of impurities and alternative chemistries on structure and properties. In addition, the information from nanoscale models represents an important source of inputs for models at larger length and time scales where engineering properties can be directly calculated. Therefore, we expect that these efforts will enable more scientifically based and reliable measurement

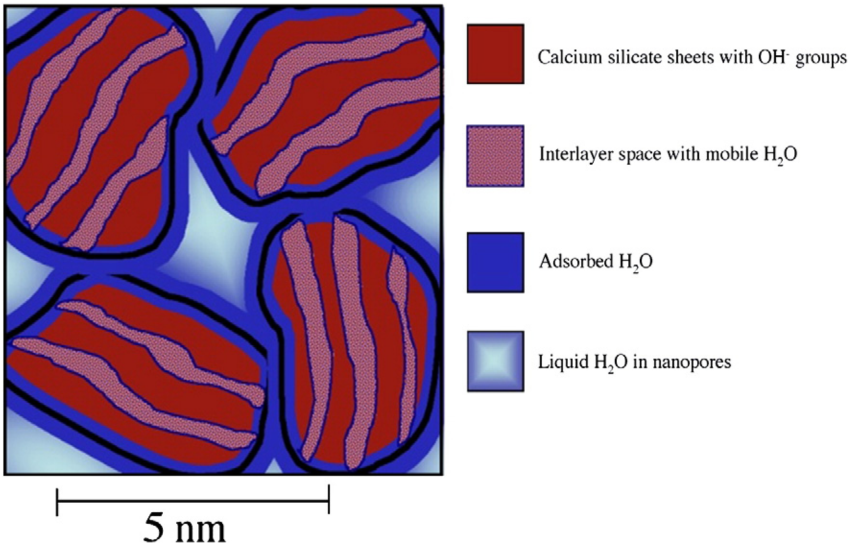

Fig. 4. New model for the structure and packing of C–S–H nanoparticles and associated water, adapted from Ref. [18].

methods that will be used to inform the development of new and more effective engineering codes, test methods, and specifications.

4. Scaling up

Despite these important advances at the bottom, the engineering behavior of a structural element is dictated by interactions among the material constituents at far greater length and time scales. To capture larger-scale behavior, microstructure and macrostructure models that employ theoretical principles such as percolation theory, effective medium theory, irreversible thermodynamics, and simulation of reaction–transport systems all can be brought to bear, as described in Ref. [29]. Microstructure models fall into one of two broad categories. In one category are models that simulate the details of coupled nonlinear chemical reactions within the microstructure that continually evolves in response. Examples are phase field models, which have been extraordinarily successful in simulating microstructure evolution in polymeric [30] and metallic [31] materials, and lattice Boltzmann models [32]. Neither phase field models nor lattice Boltzmann models have been applied to cementitious systems, but kinetic cellular automaton (KCA) models [33,34] are another member of this category that have. Recent results are indicating how the details of the chemical changes and microstructural evolution can be tracked in detail at length scales of 1 μm or less in cement pastes, as shown in Fig. 5 for a KCA simulation after the first few hours of hydration. Again, these types of simulations are beginning to shed light on how seemingly contradictory experimental data can be explained with reasonable mechanisms, as described in detail in Ref. [35].

Reaction–transport models like these are able to provide fine detail about the chemical changes in cement systems, resolving concentrations to 1 μmol or less with a spatial resolution of 1 μm or less [36]. A second category of microstructure-based models uses phenomenological rate laws defined by the user [37,38] to evolve microstructure without regard to individual chemical reaction kinetics [39,40]. These models tend to run faster than reaction–transport models because they ignore the fine chemical details. Models such as these have been used to generate interesting hypotheses about microstructure development [42], such as how filling of the pore space by C–S–H can govern hydration rates at early ages. By comparing simulations to isothermal calorimetry data, these phenomenological models have made a novel but largely unverified inference that the apparent packing density of C–S–H can change significantly during the course of the first several hours of hydration [41,42].

Both kinds of microstructure models just described are now reaching a level of maturity that enables them to capture realistic phenomena in hydrating cement pastes. As in the case of atomistic models, these same modeling strategies should be equally applicable to simulating later-age degradation processes. Importantly, the predicted microstructures from such models can be coupled to finite element and finite difference models to calculate engineering properties of the paste and of concrete itself [13,43,44].

Microstructure-level models, whatever their basis, require significant input about the physical and chemical properties of the constituent phases as well as information about the mechanisms and rates at which they dissolve, nucleate, or grow. To date, much of this input has not been available from experimental measurements, so

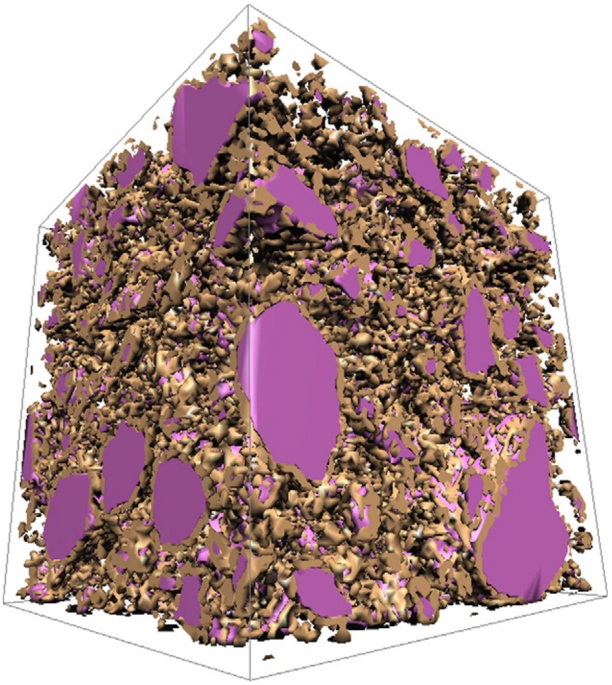

Fig. 5. Microstructure-scale simulation, using a kinetic cellular automaton model (see Ref. [36]), of the surface nucleation and growth of hydration products (brown) on cement particles (purple), showing the beginning stages of the formation of a shell of hydration product around dissolving particles.

assumptions have necessarily been made and the consequences of those assumptions have been compared to experimental observations. The problem with this approach is that there can be a multitude of required input parameters and, therefore, a multitude of such assumptions. An example, described in detail in Refs. [33,35,45] is the modeling of the initially slow reaction period during the hydration of cement paste, which has enormous consequences for predicting and controlling setting time. Even for pure C_3S pastes, a simulation of the chemical reactions and mass transport in this period requires dozens of input parameters, including the rate constants for each reaction and the properties of each component (e.g., solubility products, diffusion coefficients, molar volume, density, and stoichiometry) [33]. A further complication is that the mechanism causing the slow reaction period has not been resolved, so it becomes necessary to test each plausible mechanism for its implications about how different physical and chemical variables can influence the duration of the slow reaction period [35]. While this approach is extremely useful for gaining insights, it is difficult to have confidence in the predictive capability of simulations with multiple unverified assumptions, any one or combination of which may have significant impact on the simulated behavior.

The time is now at hand when fundamental mechanistic data obtained from calculations at the bottom scales can be integrated with these coarser models. For example, KCA models [36] have a structure and algorithms that are similar to those used by KMC (Kinetic Monte Carlo) and MD (Molecular Dynamics) models, so C–S–H composition ranges, reaction rate constants and nucleation energies calculated from KMC simulations can be incorporated almost seamlessly into KCA models to allow simulations at coarser length and time scales over which the evolution of hydrated phases or degradation processes near the surface of several cement particles can be tracked. In addition, the results at these intermediate scales can be used as “virtual experiments” to derive better phenomenological rate equations – especially for new or modified chemistries – that can be integrated in models operating at even greater scales [39].

However, this integration of models presents a serious challenge. At the microstructural scale, the molecular structure and inferred nanogranular nature of C–S–H cannot be resolved explicitly; methods are needed to enable models to communicate across radically different length and time scales. On one hand, it may be possible to summarize molecular scale structure and properties into one or more constitutive laws for C–S–H, which could then be used to model its behavior at coarser length scales. But the integration strategy may need to be more sophisticated, because C–S–H is a dynamic phase, the composition and structure of which appear able to adapt significantly to local conditions. Therefore, it is more likely that the transfer of information between models will need to be in *both* directions: (1) micrometer scale models will communicate information about local chemical, thermal, and mechanical conditions within a microstructure, (2) molecular scale models will use this information as boundary conditions for a calculation, and then (3) will communicate new information about the properties and structure of C–S–H under those conditions to the microstructure scale model.

5. Connecting the dots to design sustainable materials

Critical links between the bottom scales, as defined here, and engineering properties are still missing, both conceptually and practically. The following is just one deceptively simple yet striking example where the incompleteness of many concepts in the literature is brought into sharp relief, and how the bottom-up modeling approach can change the way new materials are adopted in our civil infrastructure.

Experiments were conducted on pastes of C_3S, of ordinary portland cement, and of white portland cement. For each type of cement, two pastes were prepared that were identical in every way except that one contained a small mass fraction of C–S–H seed particles in the mix water. The pastes were all hydrated at 20 °C. For each cement type and time of hydration, the degrees of reaction, the C–S–H mass fractions, the total porosities, and the gel–space ratios of the unseeded paste and the seeded paste were nearly the same. Despite these similarities in every macroscopic measure of the reaction progress, several engineering properties are different in preliminary tests summarized in Table 1. Although a more systematic study should be undertaken, the preliminary data indicate, for example, that the compressive strength of the seeded paste is always greater than that of the unseeded paste. The drying shrinkage, shown in Table 1 for the ordinary portland cement, is also measurably different for the seeded and unseeded paste of any cement type. But currently accepted engineering equations, such as Eq. (1) for compressive strength, relate the property of interest to a macroscopic variable such as the gel–space ratio or the total porosity, both of which are nearly the same in the seeded and unseeded pastes. Consequently, the current codes and equations that influence engineering practice simply *cannot capture the important differences* between the seeded and unseeded pastes. The main influence of the C–S–H seeds is only evident in the microstructure of the pastes, shown in Fig. 6. In the presence of seeds, the C–S–H product is more uniformly distributed throughout the microstructure and the pore size distribution is finer than in the unseeded paste. Although not reported in Table 1, these differences lead one to speculate that a seeded paste will have a lower permeability to liquid and, by inference, a greater durability than an unseeded paste.

It has been suggested that capillary pores may be estimated by weight loss when a saturated sample is dried to 85% relative humidity [46]. Again returning to the influence of seeding, Table 1 shows that the paste with greater capillary porosity and increased water loss on drying to 85% relative humidity is the sample that exhibits less shrinkage, a trend that again *is not captured by formulations that influence practice*. Without an accepted engineering code to embrace the obvious differences between these materials, and without models to assure their service life, advances of this kind are slow to be adopted in industry practice despite their evident advantages.

Many related experiments illustrate the role of pores of different sizes on both reversible and irreversible shrinkage (for example, see Ref. [9]). A bottom-up approach can help assess this situation, understand the structure–property relations and, ultimately, help inform service life models. Recent structure models of C–S–H, built at the bottom scales, have correlated surface area as measured by nitrogen adsorption and neutron scattering with packing densities of C–S–H nanogranules [16]. High surface areas are correlated with increased fractions of a low-density (LD) form of C–S–H and, therefore, decreased capillary porosity. Table 1 shows that the surface area of the seeded sample is significantly higher than that of the control. A recent analysis has shown that the volume of the smallest pores (1 nm to 10 nm) controls shrinkage; a review of the subject is included in Ref. [47]. The important point here is that this volume can be manipulated using insights obtained from fundamental simulations and experiments; this is one strategy for the design of concrete

Table 1
Comparison of properties for neat pastes and pastes seeded with C–S–H. Surface area measured by neutron scattering, with sample-to-sample variability of about 5%. 16-d compressive strength values represent the mean strength of three specimens with range of about 3 MPa. Mass loss and shrinkage values are mean values for three or four specimens of PC pastes hydrated under water for 14 d and then dried at 85% relative humidity (RH). The range in mass loss is 1% and in shrinkage is about 0.1%.

	Surface area of white PC (m^2/m^3)	16-d compressive strength of PC (MPa)	Mass loss of 14-d PC at 85% RH	Shrinkage of 14-d PC at 85% RH
Neat paste	1.23×10^6	35	6%	0.4%
Seeded paste	1.44×10^6	40	5%	0.6%

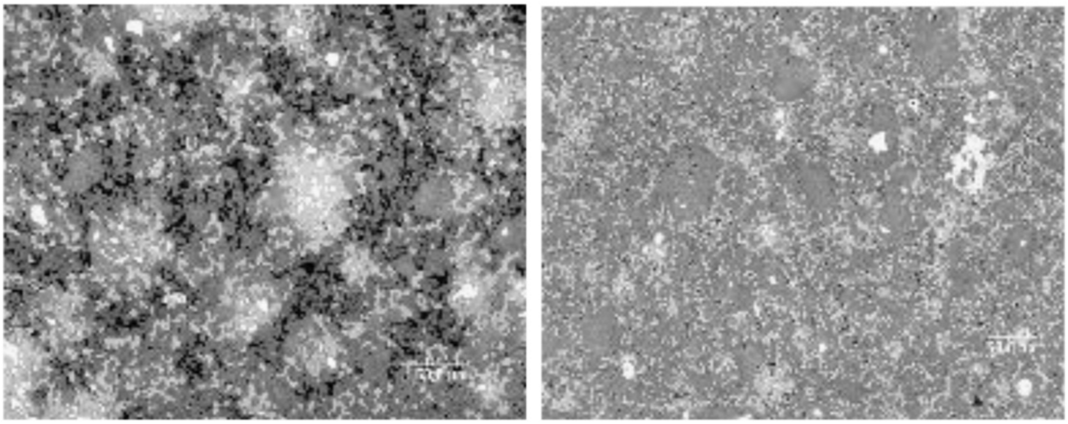

Fig. 6. Scanning electron micrographs of hydrated pastes of C_3S made without C–S–H seeding (left) and with 2% C–S–H seed particles by mass of C_3S (right), after Ref. [52].

with specific properties based on a bottom-up approach. The models of nanostructure discussed in this paper not only will reveal the mechanisms controlling the distribution of solids, but they will also offer other ways of measuring and controlling the microstructure, including, for example, shear mixing, admixtures and starting chemistry.

Pieces of a large interconnected puzzle are being developed. As described earlier, the upscaling of the complex chemical and structural interactions to length scales of micrometers or greater is a significant challenge. In the end, bulk properties boil down to explicit information about the properties of solids and interactions among solid regions and with porosity at every length scale.

6. Impacting engineering practice

As new materials and knowledge become available, we must find ways to ensure that they are deployed rapidly in industry to meet the continually increasing demands for sustainable construction. But contractors face high liability risks and are extremely reluctant to use materials without a proven track record for safety and assured service life. To expedite the acceptance of new materials and technologies, tools must be available to accelerate materials design and to make reliable predictions of service life. One thing we can anticipate now is the impossibility of using simple empirical equations for these tasks because they simply cannot capture the properties of all of the new materials either already being used or under development. On the other hand, it is utterly unfeasible to expect the construction industry to adopt multiscale modeling tools that require years of training and considerable computational expense to operate. A modeling framework like the one described here can be extremely useful in a laboratory environment and even in industrial R&D settings. But ultimately, to make a real impact on industry, the complex behavior of materials must be distilled into service life models that are easy to use. For this purpose, one might imagine a sustained collaborative effort in which the bottom-up approach, combining advanced experimental measurements and multiscale simulations, are used to gather and validate data on the properties, structure, and kinetics over a range of length and time scales. These data, along with their uncertainty and source information, would be systematically cataloged in a hierarchy of databases for each length and time scale. To be effective, this effort must encompass a wide range of material compositions, physical characteristics, mix formulations, and curing conditions so that rapid forecasts can be made for any likely field situation. Armed with this repository of data, together with rapid sub-models for synthesis and interpolation of results, simple desktop computer applications or spreadsheets with user-friendly software interfaces could then be designed as a front end for mining the database for a given application. For example, one might use the front end to input information available to the engineer about the current materials being used, similar to what is found on mill sheet specifications for each material, as well as the mix formulation, curing conditions, and geographic location of the construction. This input would be processed by the application and used to direct the database search, returning information such as the workability, the projected setting time, potential for cracking, and estimated service life at that location based on historic weather patterns mined from a database using the geographic input. For this purpose, it is critical that the databases capture the uncertainties in their data so that uncertainty can be propagated up through any intermediate equations for relating and synthesizing the data, giving traceable confidence intervals for each prediction. Only when this is done can the engineer make informed decisions about material choices.

7. Outstanding questions

Multiscale modeling approaches, already known to be effective for understanding complex behavior for other types of materials, are now being adapted and aimed squarely at understanding, predicting, and designing concrete materials. The following unanswered or controversial questions are among the most important issues that currently limit our ability to engineer concrete from the bottom up. They can and should be effectively addressed by a truly interdisciplinary approach whereby modeling and simulation are conducted alongside novel experimental measurements.

1. *What are the physical and chemical properties, and packing arrangements of C–S–H nanoparticles in various chemical environments?* Essentially all mechanical properties depend on a combination of the properties of the solid and on the volume and properties of the aqueous phase. If C–S–H is a granular solid, cohesion and friction between particles should control its viscoelastic properties. These properties must be established for the full range of C–S–H chemical compositions that can form.
2. *How does cement paste deform at the nanometer scale?* The mechanisms of irreversible deformation during drying and under load are not known, but may be related to the movement of C–S–H nanoparticles according to the nanogranular model. In that case, the integration of structural models describing the nanostructure with granular mechanic models holds significant promise.
3. *How does hydration product bond to itself and to other materials?* Concrete is a multiphase material with properties that depend on the bonding between phases. In particular, the cement paste bonds directly to aggregate. This is an under-studied question that is directly related to strength development. It is also related to cracking due to chemical shrinkage stresses and loading.

4. *What is the best quantitative description of capillary porosity?* The connectivity of the pore system determines the permeability and diffusivity of cement and concrete, which are major factors in determining durability. More detailed and comprehensive measurement strategies for the pore system in concrete must be established before better correlations between porosity and permeability can be formulated.
5. *What are the mechanisms that control the kinetics of hydration and product formation? How does the hydrated microstructure form over time? Why do some minerals react faster than others?* Relationships between the rates of hydration reactions and the resulting microstructure – and thus the ultimate properties – have long been recognized in the literature, although with little mechanistic understanding. Recently some important details regarding the relationship between kinetics and packing of particles have been established. This work needs to be extended to account for a wide range of concrete compositions. In addition, there is a great need to understand the influence of chemical admixtures, particularly polymers, and other variables with the goal of controlling properties through chemistry.
6. *What are the appropriate constitutive laws for cement paste and concrete?* The full and robust materials science approach to modeling properties depends on relationships between structure, properties, and processing based on fundamental physical principles. This approach must be followed to ensure that properties of more sustainable concrete can be predicted for reasonable ranges of all its variables and in a multitude of environments.
7. *How do polymers interact with hydration products?* Beyond understanding the effects of polymers on kinetics, there is also strong motivation to optimize the structure of C–S–H. By incorporating organic or inorganic polymers into the interlayers between sheets of C–S–H, we expect that significant modifications of macro and microproperties of C–S–H can occur.
8. *How do various chemicals attack and change the nanostructure and microstructure?* These are questions directed to durability. Sulfate attack and the interaction of alkali with various silicate minerals and aggregate are most important and should be addressed first.
9. *What are the fates of impurities?* Cement is manufactured from natural materials as they are mined from the ground, with variable types and concentrations of impurities. On occasion, impurities are present or are added with other materials such as fly ash and slag. The location of these impurities in the molecular structure, as well as their mobilities, has important consequences not only for strength but for chemical interactions with ground water in surrounding soils. This is especially important for impurities that represent health hazards such as heavy metals and radionuclides.
10. *What physical parameters can be measured to validate models and predict properties?* Quantitative analysis of micro and nanostructure of cements has not reached the same standard as has been achieved for metals and other materials. Recently developed techniques have added to the information obtained over the last 50 years or so [9], but piecing together the structure for neat portland cement has been tedious. Techniques must be developed that allow a characterization of structure in much greater detail than is possible from ordinary micrographs. Answering this question will enable these new techniques.

8. Conclusion

The bottom-up approach offers the opportunity to truly map out the structure–property–processing relationships in a fundamental, mechanistic way that will have far-reaching benefits as it matures. First, where the development of new, greener materials is currently being accomplished by trial-and-error methods, the bottom-up approach will provide a platform for extrapolating our understanding to new material chemistries and rapidly exploring the most promising formulations. Second, by distilling this mechanistic understanding into constitutive laws for relating structure and properties to processing conditions, new tools will be made available in the form of efficient design and performance models that can be adopted quickly by industry and government. To achieve this, we need correct basic principles *and* validation against measurements for material combinations that are of direct concern to industry.

Engineering concrete from the bottom up is not a mere academic exercise. It is a significant shift in the paradigm of concrete materials development, the only viable alternative to the empirical, trial-and-error methods that are now prevalent in nearly every sector of the concrete industry, and will enable that industry to be more agile as it responds to the need to offer more sustainable alternatives to traditional concrete formulations.

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