

Virtual Testing of Cement and Concrete

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Introduction

CONCRETE IS A UNIQUE MULTI-PHASE, RANDOM, complex, and composite material that provides both strength and impermeability to engineered structures. Unlike most construction materials, the properties of concrete continue to develop over time and in place—an aid in processing, but a complication in testing and quality assurance. This is clearly exemplified by the bread-and-butter test of concrete quality compliance, the 28 day compressive strength test. Having to wait 28 days to assure performance compliance is another unique feature of concrete, and not necessarily an attractive one. This holds true both for the field engineer, who would prefer to directly proceed with further aspects of the construction, and the industrial or academic researcher, who would prefer to avoid waiting 28 days (or more) before truly knowing the effects of a new chemical additive or an alternative processing methodology. Thus, many efforts have been made to predict (and ensure) concrete performance based on waiting periods of less than 28 days.

One area of effort has been the development of computer models to predict cement and concrete properties via virtual testing. In these models, typically, starting materials are characterized in some fashion and this information is input into one or more computer models to predict a variety of properties of the fresh and hardening cement or concrete. If properties can be successfully predicted, the time and cost savings to the cement and concrete industry can be tremendous. Many companies spend millions of dollars per year on the testing of concrete, including material costs, storage, labor, and disposal. An additional benefit of virtual testing would be the capability to rapidly perform a large number of “what-if” type computations to explore new material systems and optimize existing ones. With this goal in mind, in January of 2001 a joint industry/government consortium was initiated to develop a web-based Virtual Cement and Concrete Testing Laboratory (VCCTL). An earlier version of the VCCTL, 1.1, is available for the general public at <http://vcctl.cbt.nist.gov>. The progress of the consortium can be seen in three annual reports [1–3], and in numerous examples of properties that can be successfully predicted using the VCCTL [4] and other existing models.

While at first glance, it may appear that virtual testing has the potential to eventually eliminate physical testing and its

accompanying standards, the truth is that a functional VCCTL places a greater burden on testing and standards than ever before. First, model property predictions can only be as good as the characterization of the starting materials. Thus, standardized methods for preparing and analyzing these materials will be critical. And second, measurements of fundamental properties are needed in order to empower and validate the prediction models. The VCCTL will drive the standard tests to move from empiricism towards a firm materials science basis, not eliminate them. Standards and testing are critical for validating and extending the computer models. While current models can predict several properties that are already covered by existing ASTM C01 (Cement) and C09 (Concrete) standards, they can also quantitatively predict other properties for which no standard test method currently exists. Even though much work remains to be done on refining and extending these models, it is just as critical that the necessary standards work be pursued and completed. The dual objectives of this chapter, then, are (1) to show what current models can do, and (2) to highlight needs relative to existing and future standards for characterizing cement and concrete materials and for evaluating their properties.

What Really is Virtual Testing?

“Virtual testing” is an exciting name, given the ubiquity of “virtual” everything around us these days, but what does it really mean for cement and concrete materials? In the field of condensed matter physics, material properties are measured at a fundamental level. These measurements are then compared to quantitative predictions from condensed matter theory that is based on valid mathematical principles and atomic and molecular arrangements. “Simple” materials are usually studied. In materials science, more complex materials are studied, like random composites and biological materials. For many of these materials, it is not possible to carry out analytical calculations and so the field of computational materials science has been developed. All this entails is the usual condensed matter theory, but with the mathematics solved on a computer, since the problems are analytically intractable. Cement and concrete are complex, multiscale materials. The chemistry of cement is well developed and quite fundamental and analytically based, but analyzing and predicting the materials science properties requires a level of theory involving computational materials science. So the

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definition of virtual testing of cement and concrete is just the computational materials science of cement and concrete.

The ideal model for concrete would start from the known chemical composition of the material. Starting with the correct proportions and arrangement of atoms, it would build up the needed molecules, the nanostructure and microstructure needed, and eventually predict properties at the macroscale. Even with modern-day computers, however, this ideal model is a long way away. It is still not possible to systematically build up multiscale models starting from the atomic scale. The science-based virtual models that do exist need good data as input, data from careful characterization of materials. The models can predict physical properties of interest to actual materials users, but are based on fundamental parameters, not empirical tests. For example, measuring the Blaine fineness (using ASTM Standard Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus (C 204)) as a characterization of a cement does not give useful data for a model. On the other hand, careful measurement of the cement particle size distribution (PSD) does give information vital to the successful modeling of how the cement hydrates and develops microstructure. So the rise of virtual testing in this instance should drive the testing of Blaine fineness toward the measurement of cement particle size distribution. Analogous examples, in which virtual testing could push existing test methods toward more fundamental measurements, could be given in the areas of rheological properties and durability.

The Importance of Materials Characterization

The heart of concrete, as well as the heart of its virtual testing, lies in the cement. The VCCTL models start at the level of the cement particles. Specific needs are what cement particles look like, how the various chemical phases of the cement are distributed in the cement particles, what their particle size distribution is like, and what is their shape. By saying "cement," gypsum is also included since it is almost always interground with portland cement. If there are other mineral admixtures, such as fly ash, ground granulated blast furnace slag, metakaolin, silica fume, or something else, the same kind of information is needed about them as well.

To characterize a cement so that one has a hope of predicting its hydration and general performance, one must first measure the particle size distribution using some method. By far the most popular method among cement companies and other laboratories is the laser diffraction method [5,6]. This technique uses optical laser light diffracting from the various cement grains to measure/compute an equivalent spherical diameter for each particle. This is critical for virtual testing, since smaller cement grains hydrate faster and more completely than larger cement grains, having more exposed surface area, a phenomenon that must be captured accurately for any model to have a hope of being accurate. A measurement such as Blaine fineness, while useful in conveying information about the relative fineness of the cement, does not give the distribution of sizes. The hydration performance of a cement couples more to the distribution of sizes, not just some measure of the average size. In modeling the hydration of a cement, a 3-D model of the particles themselves is built up, so an accurate size distribution is needed.

Accurate bulk measures of cement chemical phases using Rietveld analysis of X-ray diffraction data, combined with particle size distribution information, can probably capture most of the information needed for experimental characterization

of a cement's hydration properties. There is work in ASTM subcommittee C01.23 at present on replacing the inaccurate Bogue calculations with more accurate X-ray diffraction Rietveld measurements [7]. But the hydration of a cement takes place at the individual particle level, so to model the hydration, one must go to the particle level. Correct particle level information is needed as an input into the virtual hydration model, CEMHYD3D [8-10].

Particle level information includes the detailed breakdown, per particle, of the various clinker phases. In a cement, some particles are purely C_3S , for example, while others are a complex mixture of clinker phases. To acquire this information, a dry cement powder is mixed into an epoxy and cured. A polished section is prepared, and a combination of back-scattered electron scanning electron microscopy (SEM) and X-ray microprobe analysis are used to identify the chemical phase belonging to each pixel in the image. This procedure is being investigated for standardization within ASTM subcommittee C01.23. Figure 1(a) shows the ordinary gray-scale back-scattered electron SEM image for a portland cement, while Fig. 1(b) shows the image after all of the major chemical phases have been identified. More details on this procedure are available elsewhere [8,11,12]. This procedure can identify calcium sulfate, but cannot distinguish between its different hydrated forms. Quantitative X-ray diffraction or thermogravimetric analysis [13] can give this information in bulk, but not at the particle level. In addition to the measurement of bulk volume fractions, the final segmented SEM images can also be analyzed to determine phase surface fractions and autocorrelation functions. Along with a measured particle size distribution, these three characteristics can be utilized to reconstruct an initial three-dimensional microstructure of cement particles in water that is a very realistic representation of the specific cement in question [8,10]. This is a critical step in the successful simulation of cement paste microstructure and performance properties. Mineral admixtures need to be characterized in the same way. A few forms of fly ash and slag have been so characterized [14,15], though further research on better adapting the above characterization techniques to these materials will prove fruitful [16].

Cement particle shape is important, too. The characterization technique for cement particle shape is very similar to that for aggregates, so aggregate shape is considered first. Aggregates used in concrete, both fine and coarse, are of many different mineralogical types, and are either found naturally in the desired gradation, or are crushed to the desired sizes. Their shape, which is measured in the ASTM Standard Test Method for Flat Particles, Elongated Particles, or Flat and Elongated Particles in Coarse Aggregate (D 4971), can vary greatly. The amount of internal porosity and hence water absorption can vary as well. Their different mineralogical types imply that their elastic moduli will also vary. To make a virtual concrete, one must in general use realistic aggregates. For some properties, like chloride diffusivity, the shape of model aggregates used does not seem to matter much. For other properties, like fresh concrete rheology and mechanical properties, especially at early ages, aggregate shape means a lot. There are few standard tests that address aggregate shape (ASTM D 4971 and ASTM Standard Guide for Petrographic Examination of Aggregates for Concrete (C 295)), and none that attempt to characterize the full 3-D aspects of shape, which must be used to understand and predict the effect of shape on properties.

To be able to build models using real-shape aggregates, one must be able to treat a given aggregate particle as a

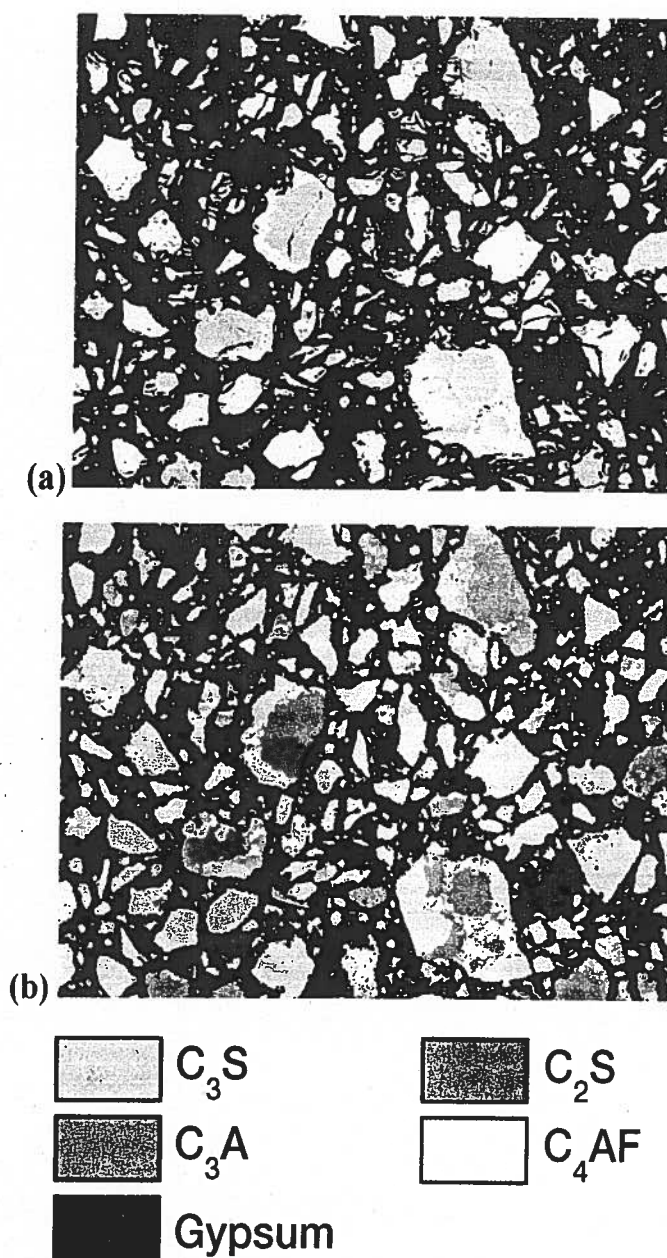


Fig. 1—(a) Backscattered electron SEM image of a cut and polished section of cement 140 from the Cement and Concrete Reference Laboratory proficiency sample program. (b) False gray scale image of the same section, based on X-ray microprobe analysis. The meaning of each gray scale is indicated in the accompanying legend. Images are $256\ \mu\text{m} \times 200\ \mu\text{m}$.

mathematical object. Spheres are easy to use, since there is a simple equation that defines their surfaces: the distance from the center of mass to the surface is a constant. Real-shaped particles can also be characterized in terms of mathematical functions, although this is a little more complicated. A recent paper [17] showed how a combination of X-ray computed tomography (CT) and spherical harmonic functional analysis could produce an analytical function for the surface of an arbitrary aggregate particle. Once this mathematical function is ob-

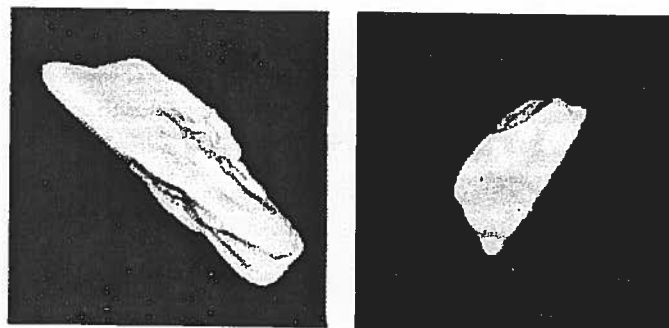


Fig. 2—Reconstructed images of aggregates sampled from AASHTO Materials Reference Laboratory (AMRL) proficiency sample #39. The left image is of a coarse limestone aggregate with an equivalent spherical diameter of 13.80 mm, and the image on the right is of a fine limestone aggregate with an equivalent spherical diameter of 1.46 mm.

tained, then real-shaped particles can be handled in a model with the same ease as spherical particles. Figure 2 shows a VRML (virtual reality modeling language) picture of a fine and a coarse limestone aggregate, from an American Association of State Highway and Traffic Officials (AASHTO) Materials Reference Laboratory (AMRL) proficiency sample. Aggregate databases are currently being built up for various aggregates and incorporated into the VCCTL.

To characterize cement particle shape requires X-ray microtomography, which can achieve the length scales of approximately $1\ \mu\text{m}/\text{voxel}$ necessary to capture the shape of particles the average size of which are usually about $10\ \mu\text{m}$ to $20\ \mu\text{m}$ [18]. A voxel is a small cubic or rectangular parallelepiped-shaped element of a 3-D digital image. After such an image is obtained, the same methods used to characterize the shape of aggregates can be used for the cement particles [19].

Virtual Testing of the Rheology of Fresh Cement and Concrete

Rheology of concrete is the study of how concrete flows, before the setting point is reached. This is important because the concrete must be placed by some kind of pouring or pumping into the prepared forms. The slump test specified in the ASTM Standard Test Method for Slump of Hydraulic-Cement Concrete (C 143/143M) is an empirical measurement of how concrete flows in a given situation. However, work in the last few decades has shown clearly that concrete rheology is characterized by at least two parameters, yield stress and plastic viscosity. In a similar way, an elastic solid is characterized by two parameters, Young's modulus and Poisson's ratio. Typically, only the Young's modulus is considered, but really both are needed to completely understand and predict the elastic performance of an elastic solid. In the same way, the slump test only measures one parameter, the yield stress, but the plastic viscosity is needed as well to be able to fully understand and predict the rheology of concrete, which in turn determines the workability and flowability of the concrete into a form or through a pumping process.

Because concrete is a multi-scale material, investigating the rheology involves a multi-scale approach. Rheology of the

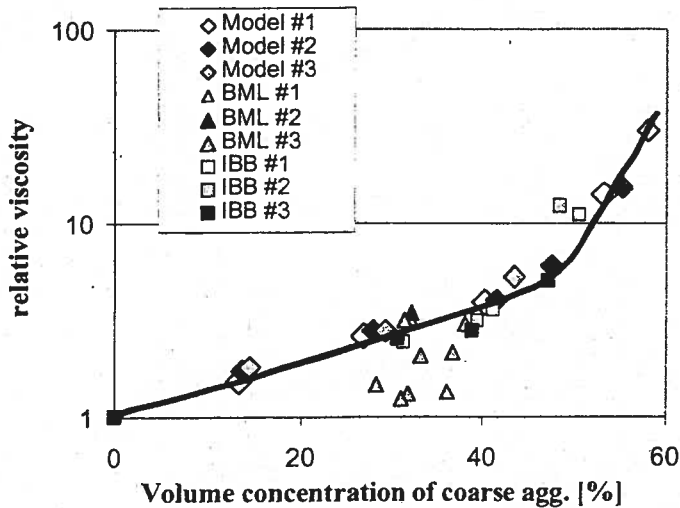


Fig. 3—Comparison of DPD model to experimental data on the dependence of relative viscosity of fresh concrete on the volume fraction of coarse aggregate. The first three sets of data in the legend are the simulations, and the remaining datasets are experimental data obtained using various rheometer types. See Ref [21] for detailed discussions of these concrete rheometer types.

cement paste greatly influences the time-dependent rheology of the concrete, and is itself non-Newtonian and complicated. However, having such a large volume fraction of aggregates, 60 % or more, also has a very large effect on concrete rheology.

Simultaneous modeling of the hydration process and cement paste rheology is beyond current computational capabilities. Therefore, we have taken a combined theoretical-experimental approach. Cement paste and mortar rheology is measured in a custom rheometer [20]. The effect of coarse aggregates on concrete rheology is modeled using a dissipative particle dynamics (DPD) approach. This is similar to a molecular dynamics approach for the movement of atoms and molecules, but adapted for coarse aggregate-size particles. The rheological properties of the matrix of the suspension come from the cement paste and mortar measurements. Figure 3 shows experimental and DPD simulated plots of the plastic viscosity of a concrete plotted versus the volume fraction of aggregate. Adding more aggregate clearly increases the apparent viscosity.

Experimentally, research is being done on measuring concrete rheology using various concrete rheometers. Several different designs are currently available. An intercomparison effort is underway [21,22], and it may be possible to extract fundamental rheological parameters (plastic viscosity and yield stress) from these measurements. This would both enable the rheological models to be validated and, more importantly, begin to allow fundamental rheological parameters to be used in analyzing and predicting concrete flow in field conditions. The DPD simulations can be used to analyze flow in different rheometer designs and extract fundamental parameters from empirical test results. There has also been DPD modeling work of concrete flow in self-compacting concrete (SCC) empirical tests, thus offering the potential for putting these tests on a more fundamental materials science basis. Some of these tests are currently being considered for standardization in ASTM subcommittee C09.47. Figure 4 shows a DPD simulation of coarse aggregate falling through four parallel rebars, similar in

some ways to the SCC tests being considered for standardization. The coarse aggregate shapes were taken from the shapes of real aggregates, characterized by the process described in the previous section.

Virtual Testing of the Properties of Hardening Cement Paste and Concrete

Hydration and Degree of Hydration

To model the development of cement and concrete properties over time, a proper understanding (and model) of the hydration process is essential. While a complete understanding of cement hydration is still lacking, a significant knowledge base [23] has been accumulated in over 100 years of experimentation. The two most influential parameters for the properties of cement and concrete are water-to-cement mass ratio (w/c) and degree of hydration. If degree of hydration (of both cement and pozzolans) can be accurately predicted, many properties can be conveniently computed, as will be demonstrated in the subsections that follow. To model the increase in degree of hydration with time, two approaches are possible, depending on whether or not the underlying (blended) cement paste microstructure is explicitly considered.

The first approach consists of utilizing some functional form to describe the relationship between degree of hydration and time. The dispersion models of Knudsen [24,25] or the use of nuclei-growth models [26] are examples of this approach. In this approach, the parameters obtained from fitting the experimental data may or may not have physical significance. In addition, prediction of the performance of other systems (change in cement composition, PSD, w/c , etc.) based on the fitting of one (or more) set(s) of experimental data may or may not be possible. Still, these equations can be useful, as they usually do provide an excellent fit to an individual experimental dataset, and thus could be used to predict later-age degree of hydration from early-age measurements.

The second approach attempts to make greater use of the detailed characterization of the starting materials described above by directly modeling the microstructure development of the cement paste. In this approach, cement PSD, phase composition and distribution, and w/c can all be explicitly considered. In the last 15 years or so, significant developments have been made in this approach, concurrent with the vast increases

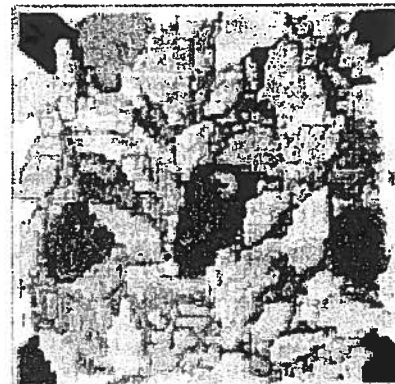


Fig. 4—Static image from simulation of vertical flow of a concrete with real particles through a grid of four steel reinforcing bars which are separated by a distance of 200 mm. The particles are dropping down, due to gravity, through the rebars.

in computer speed and available memory. A pioneering effort in this field was the work of Jennings and Johnson [27], who modeled the cement powder as a collection of spherical particles of tricalcium silicate that resulted in the formation of calcium hydroxide and calcium silicate hydrate reaction products, while explicitly considering the PSD of the powder. Similar models continue to be developed and utilized to this day [28,29]. In the early to mid 1990s, three other research groups, all active at the present date, initiated research on this topic. In Japan, Maekawa et al. developed the DuCOM (durability model of concrete) model, including modules for hydration, microstructure formation, and heat and mass transport [30]. The underlying hydration model, while focused on heat generation and water consumption, also considers the stereological aspects of the overlapping hydrating cement particles. A demonstration of the model is accessible over the Internet at <http://concrete.t.u-tokyo.ac.jp/en/demos/ducom> (accessed March 2005). In the Netherlands, van Breugel published his Ph.D. thesis [31] on the HYMOSTRUC model for the hydration and microstructure development of cement paste. This model considers the cement particles to be spherical and explicitly analytically accounts for the overlap of hydration products as the individual cement particles expand during the hydration process. The model has been applied by van Breugel and his subsequent Ph.D. students to predict a variety of cement and concrete properties, including heat development, strength development, and autogenous shrinkage [31–33].

During the same time period, Bentz and Garboczi initiated a cement hydration modeling effort [34] at the National Institute of Standards and Technology (NIST) that ultimately culminated in the CEMHYD3D three-dimensional cement hydration model [8–10]. Unlike the other models mentioned previously, CEMHYD3D considers the cement particles at the sub-particle level, applying a digital-image-based approach to the modeling of cement hydration and microstructure development. Each digitized spherical cement particle is composed of one or more digital elements (voxels) that can be assigned to be any of the possible phases of the starting cement powder. Using computational algorithms, the user is able to create an initial three-dimensional cement (in water) microstructure that matches the following measured features of the real cement powder, obtained via the characterization methods outlined earlier in this chapter: PSD, bulk phase composition, and intra-particle chemical phase distribution. An image of a portion of a typical starting 3-D microstructure is provided in Fig. 5.

In CEMHYD3D, a cellular automaton-like computer algorithm is used to simulate the hydration process. Individual cement phase voxels can dissolve, diffuse within the available capillary porosity, and react to form solid hydration products. The model proceeds as a series of dissolution/diffusion/reaction cycles, and a single user-provided parameter is used to approximately convert between hydration cycles and real time. The algorithms are applied so as to maintain the correct volume stoichiometry for the generally accepted reactions of cement hydration [8,10,23], including the chemical shrinkage first highlighted by Le Chatelier over 100 years ago [35]. Degree of hydration, of the cement powder or any combination of the original cement phases, can be determined by a simple voxel counting algorithm, either on a mass or a volume basis. CEMHYD3D has been utilized, worldwide, by cement researchers to predict performance properties and to generate microstructures for the subsequent evaluation of degradation [36–41]. In addition to cement hydration reactions, the most re-

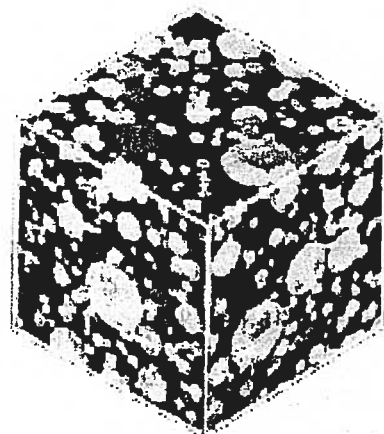


Fig. 5—Typical 3-D reconstructed microstructure used as input for the CEMHYD3D cement hydration model. The phase designated by each gray scale is shown in the legend accompanying Fig. 6.

cent version of CEMHYD3D also includes reactions for a variety of mineral admixtures such as silica fume, fly ash, slag, and limestone [1–3]. Figure 6 provides an example two-dimensional image of a portion of a hydrated CEMHYD3D microstructure.

Experimentally, no ASTM standard method exists for evaluating the degree of hydration of either portland or blended cements. For portland cements, non-evaporable water content [42] is one generally accepted method for estimating the degree of hydration of the hardened paste. In this test, the mass loss of the hydrated cement paste occurring between 105°C and 1000°C (or another similar range of temperatures depending on the preference of the researcher) relative to the mass of the ignited paste (corrected for the loss on ignition of the original cement powder) provides a measure of the non-evaporable water content. Degree of hydration (0.0–1.0) is then obtained by dividing the non-evaporable water content of the specimen by that measured for a fully hydrated cement paste specimen. The value for a fully hydrated specimen can also be estimated based on the potential Bogue composition of the cement using coefficients provided by Molina and given in Table 1 [43] (the effect of the more correct composition as determined by Rietveld X-ray diffraction analysis is not known at

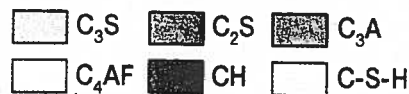


Fig. 6—2-D cross section of a 3-D model cement paste with $w/c = 0.4$, hydrated for 2000 computational cycles using the CEMHYD3D hydration model. The phase designated by each gray scale is indicated in the accompanying legend. The image is 100 $\mu m \times 100 \mu m$.

TABLE 1—Non-evaporable Water Contents for Major Phases of Cement

| Cement Phase | Coefficient (g of water per g of phase) |
|-------------------|---|
| C ₃ S | 0.24 |
| C ₂ S | 0.21 |
| C ₃ A | 0.40 |
| C ₄ AF | 0.37 |
| Free lime (CaO) | 0.33 |

present). For Type I portland cements, a typical value is on the order of 0.23 g of water per gram of cement. For blended cements, non-evaporable water content is no longer an accurate measure of degree of hydration due to the confounding influence of the pozzolanic reactions, which consume calcium hydroxide (and its accompanying non-evaporable water) in producing other cement hydration products [44,45]. The use of SEM/image analysis (e.g., point counting) to estimate the degree of hydration of both portland and blended (with fly ash or slag) cements appears to be a promising new option [46]. Clearly, this is an area where further standardization efforts are needed.

Figure 7 provides a comparison of VCCTL-predicted and experimentally measured (via non-evaporable water content) degrees of hydration for Cement and Concrete Reference Laboratory (CCRL) cement 135 with a $w/c = 0.40$, hydrated under both saturated and sealed curing conditions [47,48]. Under sealed curing conditions, the paste self-desiccates due to the chemical shrinkage that occurs during hydration, which also decreases the achieved degree of hydration at later ages. It can be observed that the computer model provides an excellent fit to the experimental data for both curing conditions, using a parameter of 0.0003 h/cycle^2 to convert between cycles and time.

Setting Time

Setting time is one of the most important properties of a cement, as it will determine how much time is available to place and finish the concrete. Two ASTM standards exist for the evaluation of setting time: ASTM Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle (C 191) and ASTM Standard Test Method for Time of Setting of Hydraulic Cement Paste by Gillmore Needles (C 266). The two usually provide slightly different values, with the Gillmore needle times for initial and final set generally being slightly greater than those obtained using the Vicat needle. Both methods basically measure when the hydrating cement paste develops some finite value of resistance to penetration.

To predict setting times using a computer model, one first needs to decide what constitutes the physical process of setting. Fundamental research has indicated that setting is normally controlled by the formation of calcium silicate hydrates (bridges) that link together the original cement particles [49,50]. In systems that undergo a rapid reaction of the aluminate phases and flash set, it is likely the aluminate hydrates that form these linking bridges. Within the VCCTL software, setting is assessed using a specialized percolation algorithm [10]. The algorithm measures the fraction of total solids (mainly cement particles at this point) that are linked together by calcium silicate hydrate gel, ettringite, and calcium aluminate hydrate hydration products. Thus, two touching cement particles are not considered to be connected, for determining setting, unless some hydration product bridges them. When such a structure spans the entire system, one says that the structure is percolated or connected or, in this case, set. In this way, the setting behavior of both well-dispersed and flocculated cement pastes can be consistently evaluated. The VCCTL program returns the percolated (connected) fraction [0,1] for the total solids as a function of either hydration time or degree of hydration.

Figure 8 shows these percolation plots versus time for CCRL cements 135 and 141 [48,51], both hydrated at a w/c determined by the ASTM Test Method for Normal Consis-

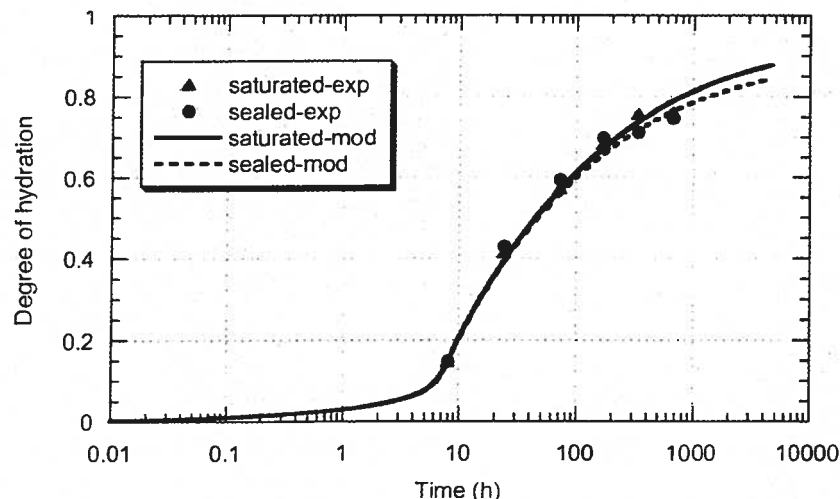


Fig. 7—Degree of hydration as a function of time for CCRL cement 135 with $w/c = 0.4$, cured isothermally at 25°C . The solid curve is the prediction by CEMHYD3D using saturated curing conditions, and the dashed line is the prediction using sealed curing conditions. The symbols are experimental measurements, based on nonevaporable water content, using saturated and sealed curing conditions, respectively. The error bars indicate \pm one standard deviation from the mean value, and are about the same size as the data symbols.

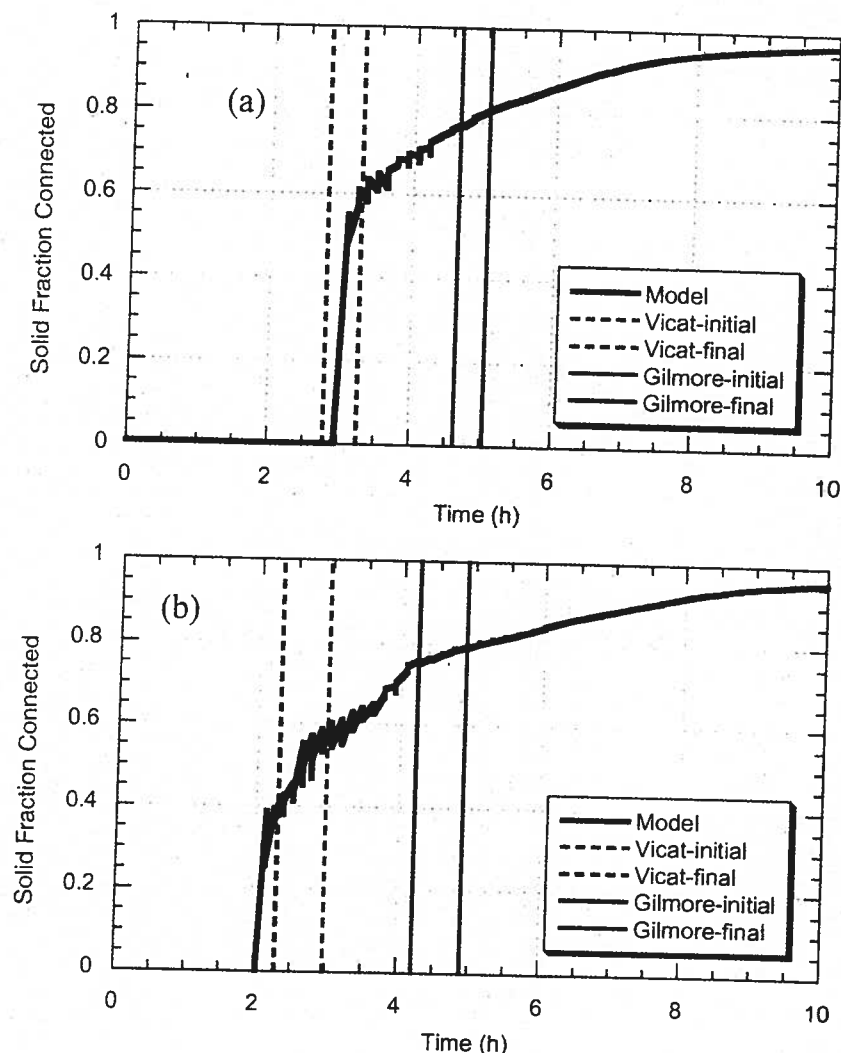


Fig. 8—Fraction of solids connected as a function of time for (a) CCRL cement #135, $w/c = 0.25$, and (b) CCRL cement #141, $w/c = 0.267$. The w/c ratio of both cements was determined by the ASTM Normal Consistency test (ASTM C 187). The fluctuations in the model curves is an indication of the randomness of the model due to its relatively small size. The vertical lines in each plot mark the measured initial and final setting times using the Vicat needle test and the Gillmore needle test. The sharp rise in the curves gives an indication of the setting times predicted by CEMHYD3D.

tency of Hydraulic Cement (C 187). The initial and final setting times as determined experimentally by both the Vicat and Gillmore needle tests are shown as vertical lines on the graphs, as noted in the caption. For the Vicat needle, the initial and final setting times are shown to approximately correspond to percolated fractions of 0.4 and 0.75, respectively. The Gillmore setting times are slightly longer, with the initial and final setting times corresponding to percolated fractions of 0.6 and 0.8, respectively. Setting time will be strongly influenced by the w/c of the cement paste and the PSD of the cement powder. As would be expected, coarser cements require more hydration time to achieve set, due to their slower hydration rate. But, these coarser systems actually achieve set at a lower degree of hydration, as fewer interparticle bridges are needed to percolate the microstructure in a coarser particle system [52].

Chemical Shrinkage

In addition to being identified by Le Chatelier over 100 years ago, the measurement of chemical shrinkage was also one of the first subjects investigated by Powers early in his career [53]. Because the cement hydration products occupy less volume than the starting materials (cement and water), a hydrating cement paste will imbibe water in direct proportion to its ongoing hydration [53,54]. This holds true except for low w/c pastes (less than $w/c = 0.4$) after a few days of curing, in which the depercolation of the capillary porosity may dramatically reduce the permeability of the cement paste and limit its imbibition rate below that required to maintain saturation during the continuing hydration [8,54]. Chemical shrinkage has been shown to be in direct proportion to other measures of degree of hydration such as non-evaporable water content and heat release [8,55]. It appears to provide a rapid method for assessing

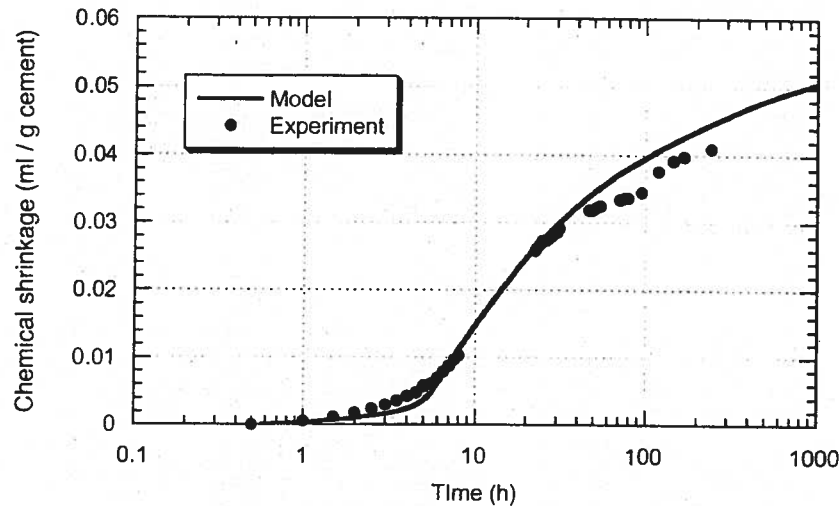


Fig. 9—Chemical shrinkage of CCRL cement 135 with $w/c = 0.3$, hydrated isothermally at 25°C under saturated curing conditions. The solid curve shows the prediction using CEMHYD3D, and the circles are experimental measurements.

early hydration rates and may provide a means for evaluating cement cracking susceptibility [56]. While no standard method currently exists for the measurement of chemical shrinkage, ASTM C01.31 subcommittee on Volume Change is currently balloting a draft standard for this test.

Knowing the volume stoichiometry (e.g., molar volumes) of all ongoing hydration reactions, it is straightforward to compute chemical shrinkage in the VCCTL CEMHYD3D model. Figure 9 provides a comparison of model and experimental results for CCRL cement 135 with $w/c = 0.3$. The deviation between model and experimental results at later ages (> 40 h) is likely due to the depercolation of the capillary porosity mentioned above, as excellent agreement is observed between model and experiment up until this time.

Heat Release and Adiabatic Temperature Rise

Another convenient measure of degree of hydration of portland cements is heat of hydration. Heat of hydration is conventionally measured using the ASTM Standard Test Method for Heat of Hydration of Hydraulic Cement (C 186). Within the CEMHYD3D computer model, heat of hydration is computed based on the individual heats of hydration of the various cement clinker (and pozzolan) phases. Knowing the degree of hydration of each individual cement phase, the overall heat of hydration is easily computed. For adiabatic boundary conditions, this heat of hydration can be readily converted to an adiabatic temperature rise, if the heat capacity, specific gravity, and mixture proportions of the concrete are known [36]. Figure 10 provides an example of the

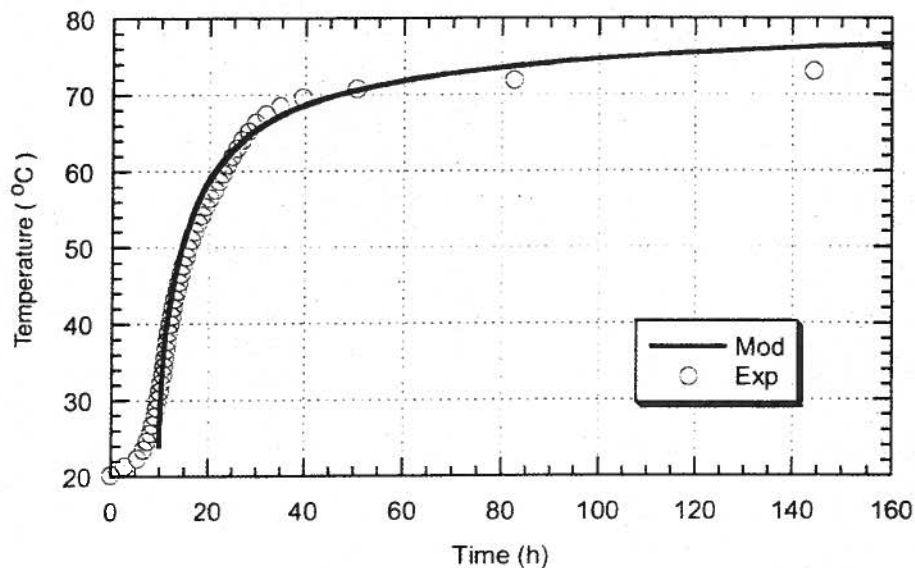


Fig. 10—Comparison of predicted (solid line) and experimental measured (data points) adiabatic heat signature curves for a $w/c = 0.65$ OPC concrete with 50 % fly ash replacement of cement, by mass.

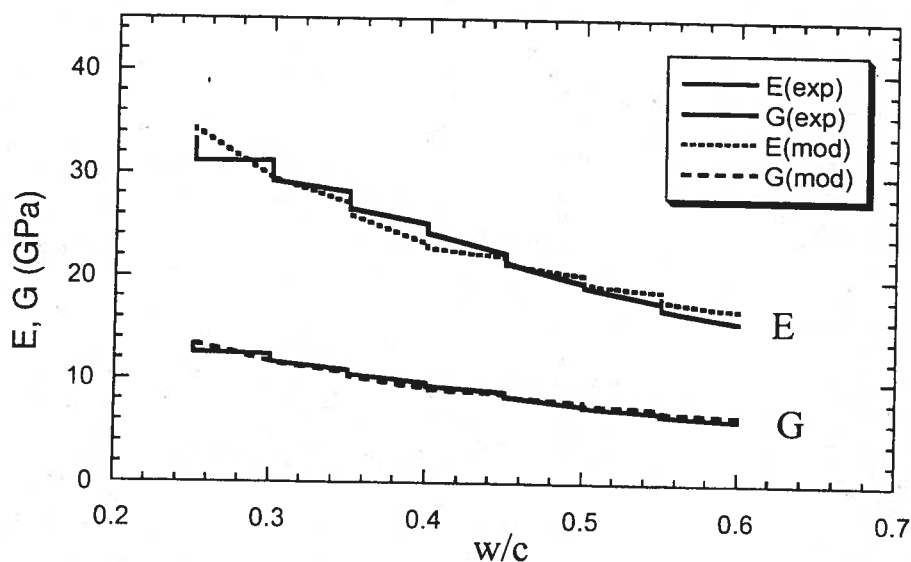


Fig. 11—Comparison of elastic moduli predictions to experimental data, versus w/c ratio, for 28-day and 56-day specimens. At each w/c ratio, the upper point is the 56-day value and the lower point is the 28-day value.

generally observed agreement between model and experimental data for the adiabatic temperature rise of a blended cement concrete.

Virtual Testing of the Properties of Hardened Cement Paste and Concrete

Elastic Moduli

As stated above, the output of the CEMHYD3D model is a digital hydrated 3-D cement paste microstructure, in which each voxel is occupied by a unique cement paste phase. By treating each voxel as a tri-linear finite element, the overall elastic moduli of the cement paste model can be computed directly using finite element techniques. A typical model is 100^3 voxels in size, so that a conjugate gradient relaxation solver must be used [57–59]. This size system can routinely be done on a modern desktop in an hour or less.

Recently, a careful test of this algorithm applied to the microstructures resulting from operation of CEMHYD3D was carried out [60]. Cement paste samples were prepared from a German cement, for w/c ranging from 0.25 to 0.6. After periods of 28 days and 56 days of curing, the degree of hydration was measured using loss on ignition (a method described above), and the elastic moduli were measured using a version of the ASTM Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Resonant Frequencies of Concrete Specimens (C 215). Figure 11 shows the comparison between model and experimental results for 28-day- and 56-day-old samples, graphed as a function of w/c. There is excellent agreement between the virtual and experimental results.

Compressive Strength

Actually, compressive strength is a more highly utilized parameter in the cement and concrete industries than are elastic moduli. Therefore, prediction of the compressive strength of mortar cubes and concrete cylinders is an obvious application for computer modeling. The compressive strength of mortar cubes is generally assessed based on the ASTM Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in. [50-mm] cube specimens) (C 109/ C 109M), while that of

concrete cylinders is assessed according to ASTM Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens (C 39/C 39M). Computationally, several approaches are possible for the prediction of compressive strength. The most widely used to date has been Powers's gel-space ratio theory [61]. In the CEMHYD3D model, voxel counting is utilized to calculate the volume fractions of "gel" and "space," and compressive strength is estimated as a function of the ratio of the two. Since a pre-factor is present in the strength prediction equation, at least one experimental measurement of compressive strength is required to estimate the pre-factor. Usually, either a 3-day or a 7-day strength measurement is performed and the resulting pre-factor is used to predict the 28-day strength. While originally developed for portland cement systems, it has been recently verified experimentally that the theory can also be applied to blended cement (specifically fly ash) systems [62]. The theory has also been used in commercially available software packages that predict compressive strength development based on the measurement of heat signature curves (as a measure of degree of hydration) [63]. Figure 12 provides an example of the agreement between model predictions and measured compressive strengths for CCRL cement 133 [10]. While it would be preferable to directly predict compressive strength development without requiring an early-age measurement, the above procedure could still result in considerable time and cost savings to the industry, as it reduces the 28-day evaluation window down to either 3 days or 7 days.

The previous subsection has illustrated that elastic moduli development can be accurately predicted using the VCCTL software. Another approach to predicting compressive strength, currently being pursued within the VCCTL consortium, is to first compute elastic moduli, and then estimate compressive strength based on some functional relationship between compressive strength and elastic modulus. A convenient empirical equation relating Young's modulus and compressive strength, based on many experimental results, is found in the ACI standards [64]. It is possible that a multiscale strength of materials theory can be formulated to give accurate, microstructure-based predictions of compressive strength via similar kinds of equations that are microstructurally based.

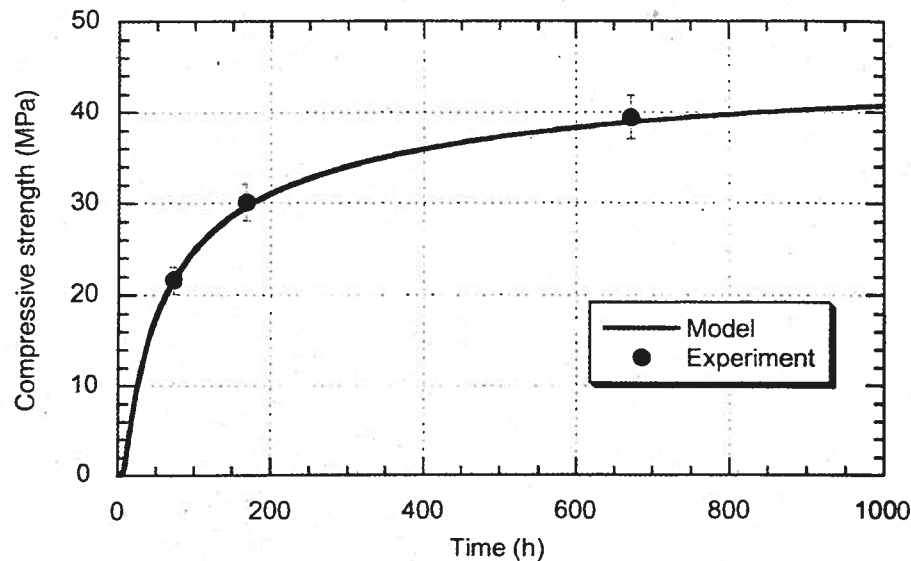


Fig. 12—Experimentally measured (circles) and model-predicted compressive strengths for ASTM C 109 mortar cubes prepared from CCRL cement 133 at 25°C. The error bars indicate \pm one standard deviation from the mean, as determined in the CCRL testing program.

Diffusivity

As more and more concrete structures are designed for durability as well as strength, transport properties such as diffusivity are becoming more important. In the past, ASTM Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (C 1202) has been used extensively to measure the "rapid chloride permeability" of a concrete cylinder. Even though the results of this test are known to be confounded by the conductivity of the pore solution and various temperature effects [65], it is still widely specified within the industry. While for a set of similar materials, the test method may produce the correct performance ranking, using the test as a performance criterion for conformance to specifications is a dangerous but ever-growing practice. The newly approved ASTM Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion (C 1556) is a welcome addition that will provide diffusion coefficients that can be subsequently used to obtain service life estimates for concrete structures. However, one has to be careful in evaluating chloride diffusion through a strong ionic electrolyte such as cement paste pore solution, and so it is possible that more refinements will have to be made [66,67].

For the case of diffusivity, successful predictions at the cement paste level have been also successfully extended to mortar and concrete [68,69]. For this application, a hard core/soft shell (HCSS) microstructural model of concrete has been developed [70]. The concrete is modeled as a three-dimensional continuum volume of spherical aggregates, in which each aggregate particle is surrounded by an interfacial transition zone (ITZ). The diffusivity of the diffusing species is different (generally higher) in the ITZ regions than in the bulk cement paste. Random walker techniques are then employed to determine the diffusivity of the overall 3-D model concrete microstructure [71]. The HCSS model is currently being extended to use real-shape aggregates instead of model spheres.

Using this approach, it has been determined that the major variables influencing concrete diffusivity are w/c, degree of hydration, aggregate volume fraction, and silica fume addition rate (other mineral admixtures have not been considered)

[68,69]. Thus, equations have been developed to predict concrete diffusivity for limited ranges of these four input parameters. It must be recognized that these equations ignore a number of field concrete realities such as (micro)cracking, partial saturation (drying), differential curing, and leaching (of calcium hydroxide) from the surface layer. While they may provide adequate predictions of the diffusivities of laboratory concretes produced under carefully controlled conditions, they should be used with caution in field applications.

Modeling the Degradation and Service Life of Hardened Cement and Concrete

An important area for virtual testing is durability, as durability-type tests are usually time consuming. Degradation mechanisms at the microstructural level have been considered, such as leaching of calcium [72], how leaching affects diffusion rates via changes in the amount and connectedness of the capillary pore space [73–76], and how leaching affects elastic moduli via the dissolution of solid phases [41,77]. Virtual durability testing is still in its infancy, however, although it will become a major area of focus as time goes on.

Prospectus and Future Directions

The previous sections have illustrated the wide variety of cement and concrete properties that can be predicted and studied using computer modeling. As computer modeling slowly moves into the industrial mainstream, new and diverse applications surely will be discovered. In addition, it has been clearly shown that standards and computer modeling can and should function in a synergistic relationship. The computer modeling efforts of recent years have clearly pointed out the need for new materials characterization standards and test methods. The models' performance depends critically on high quality input concerning the materials in question. Many of the needed new standards and test methods are already being worked on by the appropriate ASTM subcommittees.

High quality quantitative standards are also needed for the experimental validation of the computer models. Experimental validation is critical both during model development and during their extension to new systems/environments. The models can only be proved, disproved, and improved based on comparison to carefully measured quality experimental results. As the above sections indicate, computer modeling has exhibited the potential to predict a wide variety of cement and concrete properties, several of which are lacking a standard test method for obtaining the necessary experimental data. While degree of hydration, chemical shrinkage, and heat of hydration are all fundamental measures of the reactivity of a (blended) cement system, only heat of hydration is covered by an existing standard (ASTM C 186). Even this standard only provides a measure of heat of hydration at limited fixed times such as 7 days and 28 days. Both chemical shrinkage and isothermal calorimetry can provide nearly continuous monitoring of the early hydration rate of cement-based systems. For both of these measures, ASTM standard test methods would be a welcome addition to the research, production, and end-user communities. While degree of hydration by non-evaporable water content (for portland cement systems) or SEM point counting (for portland cements and those blended with slag and fly ash) typically provide measures of reactivity at limited points in time, standardization efforts for these two measures are also critically needed.

Standard test methods are lacking in a number of other areas. The results of virtual testing clearly point this out, by computing values of important parameters for which no standard measurement is available. Examples include measurement of internal relative humidity in hardened concretes, measurement of elastic moduli and creep of concrete at early ages, and mechanistic-based tests for common degradation problems such as sulfate attack and freeze-thaw degradation. In addition to its usage to predict performance properties, computer modeling should also prove invaluable in providing guidance and direction for these new standards development efforts.

Conclusion

Advances in ceramics, metals, and polymers have been driven by the development of sufficient theory to help explain puzzling experimental results and point the way to new experiments that had not been thought of previously. Theoretical (or virtual) understanding of the material gave material designers a whole new level of control over their material, leading to improvements that opened up new opportunities. Virtual testing for cement and concrete can do the same thing for these materials. Virtual testing will drive the development of empirical physical testing towards materials science-based measurements that will in turn empower the material models to have even greater predictive power and usefulness. Rightly viewed, physical testing and virtual testing are complementary, not competitive. But the development of virtual testing will drive changes in physical testing—there is no doubt about that.

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