MULTI-SCALE DIGITAL-IMAGE-BASED MODELLING OF CEMENT-BASED MATERIALS

D.P. BENTZ*, E.J. GARBOCZI*, H.M. JENNINGS+, AND D.A. QUENARD**
* Building and Fire Research Laboratory, Building 226, Room B-350, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA
+ Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208 USA
** Centre Scientifique et Technique du Batiment, Saint-Martin d'Heres, FRANCE

ABSTRACT

Computer modelling of the properties and performance of cement-based materials is complicated by the large range of relevant size scales. Processes occurring in the nanometer-sized pores ultimately affect the performance of these materials at the structural level of meters and larger. One approach to alleviating this complication is the development of a suite of models, consisting of individual digital-image-based structural models for the calcium silicate hydrate gel at the nanometer level, the hydrated cement paste at the micrometer level, and a mortar or concrete at the millimeter level. Computations performed at one level provide input properties to be used in simulations of performance at the next higher level. This methodology is demonstrated for the property of ionic diffusivity in saturated concrete. The more complicated problem of drying shrinkage is also addressed.

INTRODUCTION

Predicting the performance of concrete structures is made difficult by the complexity of the material, which has a complex microstructure [1] and exhibits composite behavior at a series of length scales. At the scale of millimeters, one can view the concrete as a composite of aggregates and air voids embedded in a continuous cement paste matrix. Even here, one may need to account for the difference in cement paste microstructure and properties in the interfacial zones surrounding each inclusion [2, 3, 4, 5, 6]. At the scale of micrometers, the cement paste is a composite of unhydrated cement particles, hydration products (crystalline and amorphous), and capillary porosity. Finally, the major hydration product of calcium silicate cements, calcium silicate hydrate (C-S-H) gel, is itself a composite of nanometer-sized "particles" and pores.

A better understanding of the physical processes occurring at each of these scales and their interactions is necessary to increase the predictability of the performance of concrete. For example, it is the capillary forces which develop in the capillary and gel pores that are mainly responsible for the drying shrinkage of concrete. Thus, to reliably predict the drying shrinkage of a field concrete, one must understand the material at the scale of micrometers and even nanometers [7]. While this large scale range cannot be easily incorporated into a single model for concrete microstructure, it is possible to develop an integrated model in

Mat. Res. Soc. Symp. Proc. Vol. 370 © 1995 Materials Research Society

Materials Research Society. Microstructure of Cement-Based Systems/
Bonding and Interfaces in Cementitious Materials, Symposia, November
28-December 1, 1994, Boston, MA Diamond, S., Mindess, S., Glasser, F
P., Roberts, L.W., Skalny, J.P., Wakeley, L.D., Editors, MRS Vol. 370
1995

which information gained at one scale level is used in computing characteristics at the next higher level [2, 8, 9], as is demonstrated in this paper.

COMPUTER MODELLING TECHNIQUES

At each scale of interest, a method for generating appropriate representative three-dimensional microstructures must be chosen. Computational techniques are then employed to compute the physical properties (diffusivity, elastic moduli, etc.) of these composite microstructures. It should be noted that application of these property computation techniques is not limited to model microstructures, as they can be equally applied to 3-D microstructural representations of real materials obtained by tomographic [10] or microscopic [11] techniques.

At the scale of nanometers, in the study described here, the C-S-H gel is modelled as a two-level structure of partially overlapping spherical particles [7]. At the macro level, the larger 40 nm spherical agglomerates shown in the top right image of Fig. 1 are each composed of smaller 5 nm diameter micro level particles, as shown in the top left image of Fig. 1. The particle sizes and the total porosity at each level have been chosen to be consistent with experimental data from small angle neutron scattering [12] and sorption measurements [13]. The models are generated in continuum space (in a three-dimensional cube with periodic boundaries) and subsequently digitized into a 3-D digital image for the evaluation of properties.

At the scale of micrometers, a cellular-automata based computer model is used to model the microstructural development of cement paste during hydration [14]. Three-dimensional versions of this computer model have been developed both for tricalcium silicate (the major component of portland cement) [15] and for portland cement, consisting of tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite, and gypsum [14]. The cement particles are modelled as digitized spheres following a user input size distribution, with the allowable particle diameter range being from about 1 to about $40 \mu m$. The hydration process is modelled in discrete cycles consisting of steps for random dissolution, diffusion, and precipitation/reaction. Volume stoichiometry is explicitly maintained by creating the appropriate number of hydration product volume units (pixels) for each cement pixel that dissolves and reacts. Three-dimensional digital-image-based microstructures generated using the models can be subsequently analyzed to determine phase percolation [16] or diffusion coefficients [17] as a function of water-to-cement (w/c) ratio and degree of hydration (α). The middle portion of Fig. 1 shows a typical two-dimensional microstructure (w/c=0.5, α=87%) generated using the tricalcium silicate hydration model. The unhydrated cement particles are white, capillary porosity is black, calcium hydroxide is light grey, and the C-S-H gel is dark grey.

At the scale of millimeters, mortar or concrete is modelled as a continuum of cement paste containing rigid (nonoverlapping) spherical [18] or ellipsoidal [19] aggregate particles following a size distribution corresponding to that of a real mortar or concrete. Each aggregate can be surrounded by an interfacial zone of some specified thickness, as shown in the bottom image of Fig. 1. Here, the aggregates are shown in dark grey, bulk cement paste is black, the interfacial zones are white, and the single rebar is light grey. One can clearly see the modification of the aggregate distribution in the vicinity of the labelled rebar as well

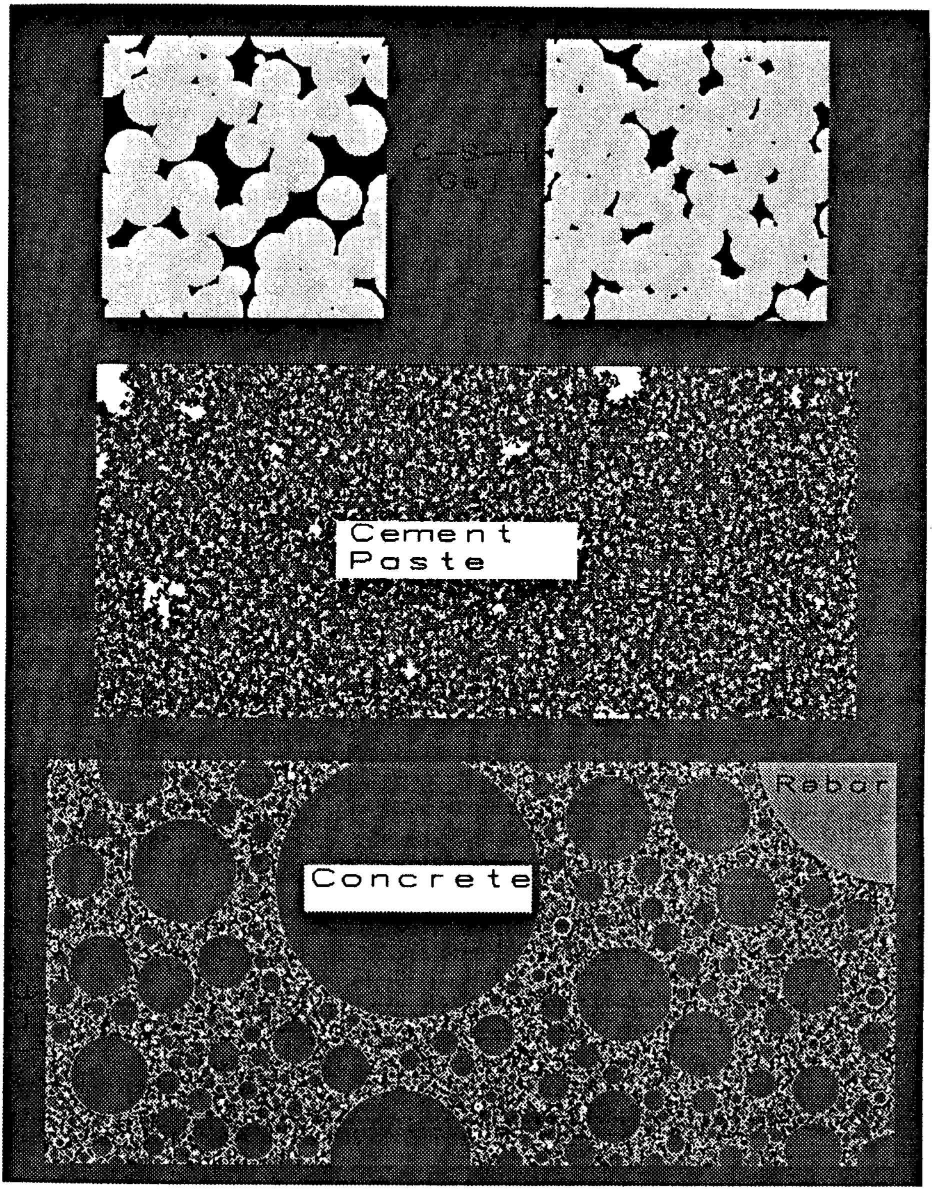


Figure 1: Two-dimensional slices from three-dimensional model microstructures of the C-S-H gel at the scale of nanometers (top image: left is micro or 25 nm by 25 nm and right is macro model or 250 nm by 250 nm), the hydrated cement paste (middle image: 250 μm by 540 μm), and a concrete (bottom image: 3 cm by 6 cm) as described in the text.

as at the top surface of the concrete and near the larger aggregate particles. Additionally, the interfacial zone cement paste is seen to occupy a large fraction of the total cement paste volume. Typically, we model mortar using a sample volume 1x1x1 cm^3, while for concrete, a sample volume of 3x3x3 cm^3 is employed. Aggregate particle diameters typically range from 75 μm to 19.05 mm (3/4"). With this range of particle sizes, a concrete simulation can require as many as 800,000 separate particles. For this reason, supercomputers are often employed for generating these structures. Once again, this continuum structure can be digitized into a 3-D digital image for the computation of properties.

Properties are generally computed using finite difference or finite element techniques [17, 20]. That is, each pixel in the 3-D microstructure is mapped into a node in either a finite element or finite difference analysis. The resultant physical equations are then solved utilizing conjugate gradient or other fast solution techniques to determine the property of interest such as an elastic modulus or diffusivity. For determining diffusivity, the Nernst-Einstein equation is used to determine the diffusivity by solving the equivalent electrical problem for the electrical conductivity of the composite material [17]. Alternatively, random walk simulations may be employed to estimate the diffusivity of a species in a composite medium, as has been utilized to estimate the diffusivity of a mortar relative to its component cement paste [3, 4, 5].

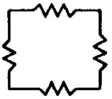
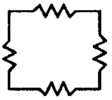
To utilize these solution techniques, the properties of each phase in a microstructure must be known or assumed. For example, to compute an elastic modulus of a cement paste microstructure, one must know the elastic properties of the unhydrated cement, the calcium hydroxide, and the C-S-H gel. Often, our approach is to utilize properties computed at one scale level of modelling as input into the computation procedures employed at a higher scale. For example, as is demonstrated in the results, the conductivity/diffusivity computed for the C-S-H gel nanostructure model can be used as an input property into the cement paste microstructure model, so that the conductivity/diffusivity of cement paste can be computed as a function of w/c and α. Likewise, the diffusivity computed for cement paste can be utilized in the model of concrete at the level of millimeters, to compute the diffusivity of a concrete, the value of actual interest to a designer or structural engineer.

RESULTS AND DISCUSSION

Transport Property Example: Diffusivity

The overall approach is demonstrated first for the case of computing the relative diffusivity of concrete. The relative diffusivity is defined as the ratio of the diffusivity of ions in a composite medium to their diffusivity in bulk water. Based on the Nernst-Einstein relation, the relative diffusivity (D/D_0) is equivalent to the relative conductivity (σ/σ_0). The results of this computation are summarized in Fig. 2, which is referred to in the discussion which follows.

The first step is the computation of the relative diffusivity of the C-S-H gel. Using the electrical analogy and the nanostructural model shown in the upper right of Fig. 1, a value of 1/300 is computed for the relative diffusivity of the gel. Here, we assume that diffusive transport occurs only in the cluster-level pores and not in the much smaller pores shown in

Scale	Computation	Relative Conductivity/Diffusivity
C-S-H Gel (Nanometers)	 Electrical Analogy	$\frac{1}{300}$
Cement Paste (micrometers)	 Electrical Analogy	$\frac{\sigma_p}{\sigma_0} = \frac{D_p}{D_0} = 0.001 + 0.07\,\phi^2 + H(\phi - 0.18)*1.8*(\phi - 0.18)^2$ $\phi = \frac{1+1.31\alpha}{1+3.2\,w/c}$
Mortar or Concrete (millimeters)	 Random Walkers	$\frac{\sigma_M}{\sigma_p} = \frac{D_M}{D_p} = 1 + c * V_{Agg} + d * V_{Agg}^2$

D_{IZ}/D_p	1	5	20
c	-1.5	-0.524	1.083
d	-0.258	0.037	0.540

Figure 2: Relative diffusivity computed using structural models at each of the three scale levels shown in Fig. 1.

the particle-level model in the upper left of Fig. 1. This is a reasonable assumption, since these smaller, nanometer size pores are on the order of the size of a water molecule and would be virtually inaccessible to many diffusing ions. A further assumption is that this relative diffusivity value is characteristic of all C-S-H gel regardless of cement composition or when during the hydration process the C-S-H is produced.

The second step is to use the value computed for the relative diffusivity of the C-S-H gel in a computation of the relative diffusivity of cement pastes of various w/c ratios and degrees of hydration. A diffusivity value of 1.0 is assigned to the capillary porosity, while the unhydrated cement and calcium hydroxide are assigned diffusivities of 0.0 since they contain no porosity. Again using the electrical analogy, computations performed for a variety of microstructures have resulted in the development of an equation which relates relative diffusivity to the capillary porosity of the cement paste as shown in Fig. 2. Good agreement has been observed in comparing these computed model values to ones measured experimentally both for chloride ion diffusivity [17, 21] and cement paste conductivity [22].

Finally, the relative diffusivity values computed for cement paste can be used as input into a structural model for mortar to determine the effect of aggregates and their surrounding interfacial zones on the diffusivity of the mortar (D_M). At this level, one must select the thickness of the interfacial zone paste and the value of its diffusivity (D_{IZ}) compared to that of the bulk paste (D_P). Fig. 2 provides equations which approximate the relative diffusivity of a specific model mortar as a function of aggregate content for three ratios of (D_{IZ}) to (D_P) and an interfacial zone thickness of $20\mu m$ [3, 4, 5]. The mortar is considered to be a model mortar in that only four different size aggregates were utilized in generating its structure. However, the computational techniques described in [3] would be equally applicable to a real mortar specimen, although the computational times will increase in proportion to the number of particles in the simulation.

Mechanical Property Example: Drying Shrinkage

The problem of drying shrinkage in concrete is much more complex from a modelling standpoint than that of ion diffusion under saturated conditions. Because much of the drying shrinkage is induced by capillary forces in the pore water [23, 24], one must be able to calculate the locations of water in a microstructure at a given relative humidity, as well as the response of this microstructure to the stresses induced by the capillary tension in the water and changes in surface energy of the adsorbed water layer [25]. A computer algorithm has been developed to simulate the adsorption/desorption of water in a two-dimensional [26] or a three-dimensional [7] porous structure based on a geometrical analysis according to the Kelvin-Laplace equation, which relates a critical pore size for capillary condensation to a partial pressure (relative humidity): $ln(P/P_0) = (2\gamma V_m)/(rRT)$. Using this equation, one can study the effects of a change in relative humidity, temperature, or liquid surface tension on the critical pore radius, r, below which capillary condensation will occur. For a fixed set of these parameters, a geometrical algorithm can be utilized to determine the locations of all liquid water in a given microstructure [7] if the drying/wetting history of the sample is known.

Once the locations of all "liquid" water in a microstructure have been determined, capillary-tension-induced stresses ($\psi = 2\gamma/r$) can be located at all solid-liquid interfaces. Then, finite element techniques can be used to compute the drying shrinkage which would be caused by these capillary forces. As shown in Fig. 3, once again, a hierarchical computation can be employed to relate the processes occurring in the C-S-H gel pores to the actual shrinkage measured on a concrete structure. At the concrete level, preliminary two-dimensional investigations have been conducted on the role of the interfacial zone in influencing elastic and shrinkage properties [6]. Depending on its local environment, at this level, one may also need to consider the distributions of temperature and moisture within a concrete structure.

CONCLUSIONS

The use of a set of multi-scale microstructural models to investigate transport and mechanical properties of concrete has been demonstrated. By relating microstructure to prop-

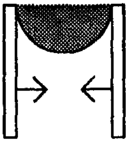
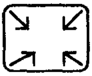
Scale	Shrinkage components	Needs
Micro C-S-H Gel	Water-to-solid interface stresses 	Elastic moduli of C-S-H particles
Macro C-S-H Gel	Interface stresses Bulk shrinkage of C-S-H agglomerates 	Elastic moduli of C-S-H agglomerates
Cement Paste	Interface stresses Bulk shrinkage of C-S-H	Elastic moduli of C-S-H, calcium hydroxide, and unhydrated cement
Mortar	Bulk shrinkage of bulk paste Bulk shrinkage of IZ paste	Elastic moduli of bulk cement paste, IZ cement paste, and aggregate Temperature, moisture distributions

Figure 3: Approach to computing drying shrinkage using structural models at each of the three scale levels shown in Fig. 1.

erties at all relevant size scales, a more complete understanding of the influence of microstructure and the underlying physical processes on the performance of these composite materials can be obtained. For the case of chloride diffusivity, a complete set of results has been presented. For the more complicated phenomenon of drying shrinkage, much work is still needed, but the basic conceptual groundwork for modelling has been developed. As the structural modelling and computational capabilities described herein continue to evolve, their use as a tool in the design of a concrete with desired properties and service life should become a reality.

NOTATION

Symbols

α - degree of hydration

γ - liquid surface tension

ϕ - porosity
ψ - stress
σ - conductivity
c, d - constants in equation to estimate mortar relative diffusivity
D - diffusivity
$H(x)$ - heaviside function = (1: x $\geq$0; 0 otherwise)
P - pressure
r - pore radius
R - universal gas constant
T - absolute temperature
V - volume fraction
w/c - water to cement ratio

Subscripts
Agg - aggregate
0 - bulk solution
IZ - interfacial zone cement paste
m - molar
M- mortar
P - bulk cement paste

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation Science and Technology Center for Advanced Cement-Based Materials for partial financial support of much of the work described in this paper.

REFERENCES

[1] Scrivener, K.L., in Materials Science of Concrete I, edited by J.P. Skalny (American Ceramic Society, Westerville, OH, 1989), p. 127.

[2] Bentz, D.P., Schlangen, E., and Garboczi, E.J., in Materials Science of Concrete IV, edited by J.P. Skalny and S. Mindess (American Ceramic Society, Westerville, OH, 1994).

[3] Garboczi, E.J., Schwartz, L.M., and Bentz, D.P., "Modelling the Influence of the Interfacial Zone on the Conductivity and Diffusivity of Mortar," submitted to *J. of Advanced Cement-Based Mat.*

[4] Garboczi, E.J., Schwartz, L.M., and Bentz, D.P., "Modelling the D.C. Electrical Conductivity of Mortar," these proceedings.

[5] Schwartz, L.M., Garboczi, E.J., and Bentz, D.P., "Interfacial Transport in Porous Media: Application to D.C. Electrical Conductivity of Mortars," submitted to *Phys. Rev. B.*

[6] Neubauer, C.M., Jennings, H.M., and Garboczi, E.J., "Modelling the Effect of Interfacial Zone Microstructure and Properties on the Elastic Drying Shrinkage of Mortar," submitted to *J. of Advanced Cement-Based Mat.*

[7] Bentz, D.P., Quenard, D.A., Baroghel-Bouny, V., Garboczi, E.J., and Jennings, H.M., "Modelling Drying Shrinkage of Cement Paste and Mortar: Part 1. Structural Models from Nanometers to Millimeters," to appear in *Mat. and Struc.*

[8] Jennings, H.M., and Xi, Y., in Creep and Shrinkage of Concrete, edited by Z.P. Bazant and I. Carol (E & F Spon, London, 1993), p. 85.

[9] Huet, C., in Micromechanics of Concrete and Cementitious Composites, edited by C. Huet (Presses Polytechniques et Universitaires Romandes, Lausanne, 1993), p. 117.

[10] Bentz, D.P., Martys, N.S., Stutzman, P.E., Levenson, M.S., Garboczi, E.J., Dunsmuir, J., and Schwartz, L.M., "X-Ray Microtomography of an ASTM C109 Mortar Exposed to Sulfate Attack," these proceedings.

[11] Stutzman, P.E., *Ceramic Trans.* **16**, 237 (1991).

[12] Allen, A.J., Oberthur, R.C., Pearson, D., Schofield, P., and Wilding, C.R., *Phil. Mag. B* **56** (3), 263 (1987).

[13] Baroghel-Bouny, V., PhD thesis, L'ecole Nationale des Ponts et Chaussees, Paris, France 1994.

[14] Bentz, D.P., Coveney, P.V., Garboczi, E.J., Kleyn, M.F., Stutzman, P.E., *Modelling and Sim. in Mat. Sci. and Eng.* **2** (4), 783 (1994).

[15] Bentz, D.P., and Garboczi, E.J., "Guide to Using HYDRA3D: A Three-Dimensional Digital-Image-Based Cement Microstructure Model," NISTIR **4746**, U.S. Department of Commerce (1992).

[16] Bentz, D.P., and Garboczi, E.J., *Cem. and Conc. Res.* **21**, 325 (1991).

[17] Garboczi, E.J., and Bentz, D.P., *J. of Mat. Sci.* **27** 2083 (1992).

[18] Winslow, D.N., Cohen, M.D., Bentz, D.P., Snyder, K.A., and Garboczi, E.J., *Cem. and Conc. Res.* **24** (1), 25 (1994).

[19] Bentz, D.P., Hwang, J.T.G., Hagwood, C., Garboczi, E.J., Snyder, K.A., Buenfeld, N., Scrivener, K.L., "Interfacial Zone Percolation in Concrete: Effects of Interfacial Zone Thickness and Aggregate Shape," these proceedings.

[20] Garboczi, E.J., and Day, A. R., "An Algorithm for Computing the Effective Linear Elastic Properties of Heterogeneous Materials: 3-D Results for Composites with Equal Phase Poisson Ratios," submitted to *J. of Appl. Phys.*

[21] Halamickova, P., Detwiler, R.J., Bentz, D.P., and Garboczi, E.J., "Water Permeability and Chloride Ion Diffusion in Portland Cement Mortars: Relationship to Sand Content and Critical Pore Diameter," accepted by *Cem. and Conc. Res.*

[22] Olson, R.A., Christensen, B.J., Coverdale, R.T., Ford, S.J., Moss, G.M., Jennings, H.M., Mason, T.O., and Garboczi, E.J., "Microstructural Analysis of Freezing Cement Paste Using Impedance Spectroscopy," submitted to *J. of Mat. Sci.*

[23] Bentur, A., Berger, R.L., Lawrence, Jr., F.V., Milestone, N.B., Mindess, S., and Young, J.F., *Cem. and Conc. Res.* **9**, 83 (1979).

[24] Fu, Y., Gu, P., Xie, P., and Beaudoin, J.J., *Cem. and Conc. Res.* **24** (6), 1085 (1994).

[25] Wittmann, F.H., in Creep and Shrinkage in Concrete Structures, edited by Z.P. Bazant and F.H. Wittmann (John H. Wiley & Sons, Ltd., New York, 1982) p. 129.

[26] Quenard, D.A., Bentz, D.P., and Garboczi, E.J., in Drying '92, edited by A.S. Mujumdar (Elsevier Science, 1992) p. 253.