

# **Diffusivity-porosity relation for cement paste**

by

**E. J. Garboczi and D.P. Bentz  
Building and Fire Research Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899 USA**

**Reprinted from Materials Science of Concrete: Sulfate Attack Mechanisms, Special Volume, Edited by Jacques Marchand and Jan P. Skalny, The American Ceramic Society, 735 Ceramic Place, Westerville, Ohio 43081. Proceedings from Seminar on Sulfate Attack Mechanisms, October 5-6, 1998, Quebec City, Quebec, Canada, 259-264 pp., 1999**

**NOTE: This paper is a contribution of the National Institute of Standards and Technology and is not subject to copyright.**

**NIST**

**National Institute of Standards and Technology**  
Technology Administration, U.S. Department of Commerce

## Diffusivity-porosity relation for cement paste

E.J. Garboczi and D.P. Bentz  
226/B350, Building Materials Division  
National Institute of Standards and Technology  
Gaithersburg, Maryland 20899 USA

### ABSTRACT

The development of a ionic diffusivity-porosity relation for cement paste, soundly based on microstructure, along with future developments in this area, are discussed. The importance of such relations for sulfate attack and other mechanisms of deterioration in concrete, as well as for models of the chloride diffusivity of concrete, are outlined.

### INTRODUCTION

The dependence of ionic diffusivity on cement paste pore space characteristics is an important quantity in modelling and understanding ionic transport through concrete. An equation for water-saturated cement paste, based on microstructural modelling, was developed several years ago [1]. This equation has since been used as the heart of a multi-scale model for concrete diffusivity [2,3], and as a key component in a sulfate attack model described in the paper by J. Marchand et al. [4] in this proceedings. The present paper serves as a supplement to Marchand's paper, and discusses the development of this equation, and present work being done to refine and extend this equation.

### DEVELOPMENT OF DIFFUSIVITY-POROSITY EQUATION

The equation to be discussed is the following:

$$D/D_0 = H(\phi - 0.18) 1.8 (\phi - 0.18)^2 + 0.07 \phi^2 + 0.001 \quad (1)$$

where  $D$  is the water-saturated bulk or effective ionic diffusivity measured by a barrier experiment, in which a slab of cement paste is used as the barrier through

---

To the extent authorized under the laws of the United States of America, all copyright interests in this publication are the property of The American Ceramic Society. Any duplication, reproduction, or republication of this publication or any part thereof, without the express written consent of The American Ceramic Society or fee paid to the Copyright Clearance Center, is prohibited

which ions can diffuse.  $D_0$  is the diffusivity of the ion in question in unconfined water,  $\phi$  is the capillary porosity, and  $H(x)$  ( $H(x > 0) = 1$ ,  $H(x \leq 0) = 0$ ) is the Heaviside function. The three terms will be discussed in detail below, once the microstructural model used to generate this equation is introduced.

The microstructure model used to generate this equation is no longer used by us in that form, although it has been incorporated into improved models [5,6]. It was a model for  $C_3S$  hydration, where the  $C_3S$  particles formed specified amounts of CH and C-S-H [1,7]. No other phases were considered. It was a cellular automaton model, as are the present models. In this model, material first dissolved from the cement grains to form diffusing species. These species diffused through the pore space, and reacted and formed C-S-H material and CH crystals. Only after every diffusing species was reacted would a new dissolution cycle begin.

After a specified amount of hydration was carried out, as determined by the degree of hydration or by the capillary porosity reached, the resulting microstructure was saved in a computer file and read into a 3-D conjugate gradient program that would solve for the effective diffusivity,  $D/D_0$ , of the structure. The capillary porosity was given a diffusivity of  $D_0$ . The C-S-H phase was considered as a solid phase that had small but finite diffusivity, which was chosen so as to roughly match experimental data. The ultimate value of the C-S-H diffusivity was taken to be  $0.0025 D_0$ . Since only the ratio  $D/D_0$  was being determined, the results were of course independent of the value of  $D_0$ . Many computations were carried out for w/c ratios ranging from 0.4 to 0.6, and degree of hydrations ranging up to 1. These data were all collected together on one graph, and showed that a universal curve could be obtained, depending only on capillary porosity, and not w/c ratio. Fitting this curve was done in steps, analyzing each part of the curve and its dependence on microstructural parameters. The three terms in eq. (1) were the result.

The first term,  $H(\phi - 0.18) 1.8 (\phi - 0.18)^2$ , came from percolation considerations. This model was found to have a critical porosity of about 18%, below which the capillary porosity became disconnected [8]. If the C-S-H diffusivity was turned off, which can be easily done in this model, then it was found that the overall diffusivity also went to zero at this percolation threshold in a power law of the difference of the porosity from 0.18, with a power of 2, in agreement with percolation theory [9]. The prefactor of 1.8 was found by fitting this data. This term was then included in the fit of the overall data, with the Heaviside function added in order to turn off this percolation term when the capillary porosity was disconnected.

The third term was determined by considering fully hydrated systems, where the main

diffusion was through the C-S-H phase. Using effective medium theory [1], it was determined that there was only a small dependence on w/c ratio at late stages of hydration, so a best-fit constant of 0.001 was used, which of course depends on the value chosen for the C-S-H diffusivity, 0.0025.

The second term,  $0.07 \phi^2$ , was chosen to connect the percolation behavior, which tends to dominate in early hydration, with the nearly constant diffusivity, which dominates the late hydration behavior. The form of this term was chosen to reflect an Archie's law-type form [1]. The value of the exponent and the prefactor were chosen from a fit to the master curve generated by simulation.

Further simulations of the C-S-H nanostructure have given values of diffusivity relative to  $D_0$  around the value of 0.0025, lending support to this choice [10], and comparisons with careful experiments on white cements (used because of similarities to pure  $C_3S$  cements) showed that eq. (1) was indeed reasonable. This equation has since been used for predicting portland cement paste diffusivity, with reasonable results [2,4], although in principle, the simulations that supplied the data for eq. (1) were only for  $C_3S$  cement pastes.

#### AREAS OF IMPROVEMENT NEEDED

Over the last six years, changes in computer memory and speed, and new knowledge, have forced us to begin re-evaluating eq. (1). These reasons are discussed below.

The original microstructure model based its volume stoichiometry for the  $C_3S$ -water reaction on work by Young and Hansen [12]. It has since been realized, by those investigators and by us, that the volume of C-S-H produced per volume of  $C_3S$  reacted, 1.7, did not properly take into account chemical shrinkage. A more correct value of this number is 1.52 [5]. Also, the original model had the dissolution and diffusion/reaction cycles occurring separately. The latest version of the cement paste hydration model has these cycles occurring simultaneously, more in accord with the real experimental situation.

In Refs. [1] and [8], a cement particle size distribution was used that we have come to realize is quite unrealistic. This was four sizes of particles, with equal numbers of all four sizes. It is much more realistic to have approximately equal masses of different size particles, so that the number of small particles is enormously larger than the number of large particles. Recent results have shown that the capillary percolation threshold depends somewhat on the particle size distribution used, ranging from about 0.18, for the unrealistic particle size distribution described above,

to 0.22 for more realistic size distributions [13,14]. The exact value of the capillary porosity percolation threshold will affect the form of eq. (1) to some extent.

Experimental evidence has shown that there are some differences, on the order of a factor of two, between white cement and portland cement pastes for the value of  $D/D_0$ , especially at late degrees of hydration [15]. The microstructural model can now do portland cement hydration, so this difference needs to be checked carefully. Also, at late degrees of hydration, the value of  $D/D_0$  obtained in the model is dominated by the value of diffusivity assigned to the C-S-H phase. This value needs to be re-evaluated as well in light of the experimental evidence and the changes in the model.

All the percolation and diffusivity work that has been done with the old microstructural model, on which eq. (1) is based, used  $100^3$  size systems, where each pixel had an edge length of one micrometer. Therefore the smallest capillary pore was of necessity one micrometer. This choice reflected the computing power of the computers available to us at that time. Computers have changed enormously over the past 6-8 years, in memory and computing speed, and so we are now able to test the percolation and diffusivity results obtained from the model at different choices of resolution, probably up to  $1000^3$  size models or a smallest pore size of 0.1 micrometers.

#### DISCUSSION

All of the improvement needs listed in the last section are being carried out at present. We would like to emphasize that we do not expect huge qualitative changes in eq. (1). In fact, the early hydration parts of eq. (1) will probably change very little. It is in the late hydration stages that improvements are needed and hopefully will be seen. At the very least, the new version of eq. (1) obtained will be on a sounder scientific footing than the old version.

Qualitatively, the present form of eq. (1) is to be expected. This is because the percolation behavior of the capillary porosity must dominate the early hydration diffusivity. The competition between the well-percolated but low diffusivity C-S-H sets the scale for the intermediate hydration stage, and the increasing C-S-H phase and decreasing, disconnected capillary porosity phase must determine the late hydration diffusivity. We hope to correct and improve the quantitative details of these stages represented in eq. (1).

Finally, a possibility should be mentioned that is at present beyond the capabilities of

our model, but may have to be dealt with in the future. That is the possibility of two kinds of C-S-H, present in different amounts and locations at different hydration times [16]. This would of course affect the diffusivity. The difficulty would be in determining the kind of C-S-H a particular pixel should be, as the diffusivities to be assigned would probably be very different. At present, since further specific information is not available, all the C-S-H in the microstructural model is given the same diffusivity. However, the model is easily capable of handling several different kinds of C-S-H, due to its cellular automaton, digital-image-based structure.

One main use of eq. (1) is as a key step in predicting the diffusivity of concrete in a multi-scale model [2,3]. In Marchand's sulfate attack model, changes in the porosity of a cement paste due to consumption or growth of various compounds change the overall diffusivity of the microstructure via eq. (1). CH leaching has a similar effect on diffusivity via changes in porosity amount and topology [17,18]. The proposed re-evaluation of eq. (1) almost certainly will not qualitatively change these results, but should introduce some quantitative changes, on the order of a factor of two, at the later stages of hydration. We have also carried out some work on modifying eq. (1) for partially-saturated cement pastes, but this work is only preliminary for now [19].

#### REFERENCES

\*Note: Refs.1,2,3,6,8,10,11,and 17 are also available on-line at <http://ciks.cbt.nist.gov/garboczi/>

- [1] E.J. Garboczi and D.P. Bentz, "Computer simulation of the diffusivity of cement-based materials," *J. Mater. Sci.* **27**, 2083-2092 (1992).
- [2] D.P. Bentz, E.J. Garboczi, and E.S. Lagergren, "Multi-scale microstructural modelling of concrete diffusivity: Identification of significant variables," *ASTM Cement and Aggregates* **20**, 129-139 (1998).
- [3] E.J. Garboczi and D.P. Bentz, "Multi-scale analytical/numerical theory of the diffusivity of concrete," *Adv. Cem. Based Mater.* **8**, 77-88 (1998).
- [4] J. Marchand, E. Samson, and Y. Maltais, "Modeling microstructural alterations of concrete subjected to external sulfate attack," in these proceedings.
- [5] D.P. Bentz, "Three-dimensional computer simulation of portland cement hydration and microstructure development," *J. Amer. Ceram. Soc.* **80**, 3-21 (1997).
- [6] D.P. Bentz, "Guide to using CEMHYD3D: A three-dimensional cement hydration and microstructure development modelling package," NISTIR 5977 (1997).
- [7] D.P. Bentz and E.J. Garboczi, "Guide to using HYDRA3D: A three-dimensional digital-image-based cement microstructural model," NISTIR 4746 (1992).
- [8] D.P. Bentz and E.J. Garboczi, "Percolation of phases in a three-dimensional

- cement paste microstructural model," *Cem. Conc. Res.* **21**, 325-344 (1991).
- [9] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).
- [10] D.P. Bentz, D.A. Quenard, V. Baroghel-Bouny, E.J. Garboczi, and H.M. Jennings, "Modelling drying shrinkage of cement paste and mortar: Part I. Structural models from angstroms to millimeters," *Mater. Struc.* **28**, 450-458 (1995).
- [11] B.J. Christensen, T.O. Mason, H.M. Jennings, D.P. Bentz, and E.J. Garboczi, "Experimental and computer simulation results for the electrical conductivity of portland cement paste," in *Advanced Cementitious Systems: Mechanisms and Properties, Vol. 245*, edited by F.P. Glasser, G.J. McCarthy, J.F. Young, T.O. Mason, and P.L. Pratt (Materials Research Society, Pittsburgh, 1992), pp. 259-264.
- [12] J.F. Young and W. Hansen, in *Microstructural Development During Hydration of Cement*, edited by L.J. Struble and P.W. Brown (Materials Research Society, Pittsburgh, 1987).
- [13] D.P. Bentz and C.J. Haecker, "An argument for using coarse cements in high performance concretes," *Cem. Conc. Res.*, in press (1999).
- [14] E.J. Garboczi and D.P. Bentz, "Re-examination of capillary porosity percolation in a cement paste microstructural model," to be submitted to *Cem. Conc. Res.* (1998).
- [15] B.J. Christensen, Ph.D. thesis, Northwestern University (1992).
- [16] C.M. Neubauer, T.B. Bergstrom, K. Sujata, Y. Xi, E.J. Garboczi, and H.M. Jennings, "Drying shrinkage of cement paste as measured in an ESEM and comparison to microstructural models," *J. Mater. Sci.* **32**, 6415-6427 (1997).
- [17] D.P. Bentz and E.J. Garboczi, "Modelling the leaching of calcium hydroxide from cement paste: Effects on pore space percolation and diffusivity," *Mater. Struc.* **25**, 523-533 (1992).
- [18] S. Rémond, "Evolution de la microstructure des bétons contenant des déchets au cours de la lixiviation," Ph.D. thesis, L'Ecole Normale Supérieure de Cachan, 1998.
- [19] N. Martys, "Diffusion in partially saturated porous materials," *Mater. Struc.*, in press (1999).