Multiscale Analytical/Numerical Theory of the Diffusivity of Concrete

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The ionic diffusivity of a concrete is a function of its microstructure at many length scales, ranging from nanometers to millimeters. The microstructure is largely controlled by the initial concrete mixture proportions and the ultimate curing conditions. Linking a property like ionic diffusivity to the microstructure then requires a multiscale approach. A multiscale microstructural computer model for ionic diffusivity has been previously developed. This model has been developed specifically to compute the chloride diffusivity of concretes with various mixture proportions and projected degrees of hydration. The three key parts of this model were dependent on large-scale supercomputer-magnitude simulations to: (1) determine the total volume of interfacial zones for a given aggregate distribution; (2) simulate the hydrated cement paste microstructure around a typical aggregate; and (3) compute the effect of the aggregates and interfacial zones on the overall diffusivity of the concrete. The key feature of this model is that one can approximately take into account the redistribution of cement paste between interfacial transition zone regions and bulk paste regions, and its important effect on overall concrete diffusivity. In the present article, we review the previously developed model and show how analytical equations can accurately replace the large scale computer simulations of parts (1) and (3). This accomplishment will make the model more usable by those who do not have access to supercomputer computing power. ADVANCED CEMENT BASED MATERIALS 1998, 8, 77–88. *Published by Elsevier Science Ltd.*

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O ne of the properties contributing to the service life of concrete structures is the resistance the concrete provides to the diffusive ingress of deleterious species such as chloride and sulfate ions [1,2]. Prediction of the diffusivity of a concrete based on its mixture proportions and expected curing is needed to help predict its service life in its expected service environment. The availability of such a prediction capability in terms of the initial mixture proportions and expected curing of a concrete will allow the rational development of durability based, in addition to the current strength based, design codes. In fact, durability specifications are already being issued, even though there has not been quantitative theory developed that can accurately predict the chloride ion diffusivity of a given concrete [3]. The model described in this article can help to overcome this barrier, even though other types of transport mechanisms, like sorption, are also important for chloride ingress [4].

Because of the wide range of feature sizes in concrete, from nanometer-sized pores to millimeter-sized aggregates, it is impossible, because of memory limitations on current computers, to simultaneously represent all of these structural features in a single microstructure model. For example, if in a three-dimensional (3-D) digital image model we let the pixel size be one nanometer, which would be barely adequate for the resolution of the C-S-H phase, then the minimum size model that would incorporate enough aggregates to be statistically valid would be at least 30 mm on a side, and contain $2.7 \cdot 10^{22}$ pixels! Uniting multiple length scales in a single model in a more sophisticated way then obviously becomes necessary.

Multiscale modeling techniques offer a promising solution to this restriction [5,6]. In this approach, properties computed at one scale, micrometers for instance, are input into a model that is constructed at a higher scale, such as millimeters. The present model combines microstructure models for the cement paste surrounding a single aggregate (micrometers) and for a representative volume of concrete (millimeters). These two microstructure models are used, in association with numerical techniques for computing the diffusivity of a 3-D microstructure, to compute the diffusivity of a representative volume of concrete. This procedure has been demonstrated previously for mortars [6]. The equation used for diffusivity at the micrometer scale also indirectly incorporates information from the nano-

meter scale, so that 6–7 orders of magnitude of length scale are actually contained in the model.

In reference [7], it was shown how to compute the overall diffusivity of a concrete model, where the difference between bulk and interfacial transition zone (ITZ) cement paste could be quantitatively taken into account. In that article, it was mentioned that the redistribution of cement between bulk and ITZ regions could very well be important and would have to be considered in future models. The main reason for this particular multiscale approach being developed [8] was to approximately handle this redistribution of cement between ITZ and bulk cement paste. This effect does indeed turn out to play an important role in predicting concrete diffusivities, because it affects what diffusivity values need to be assigned to the bulk and ITZ phases in a concrete. Therefore, the results of reference [7] are incomplete and, in general, by themselves, should not be used to analyze an experiment.

In reference [8], this multiscale modeling approach was extensively discussed, showing how different length scales could be quantitatively linked to predict the diffusivity of a concrete material. Because of the complexity of the problem, several key steps used in generating the model results had to be based on large-scale computer simulations, using supercomputer-scale computing power. Because of this approach, it was hard to change parameters, because of the long run times involved. Also, the computing power necessary to solve the model would be unavailable for most concrete technologists. In this article, we show how two of the three key steps in the multiscale model can be accurately replaced with analytical expressions. This will make the results of this model much more accessible. Previous numerical results are used to check the accuracy of this analytical replacement.

The multiscale model has some limitations. The model applies to conventional ($0.25 < \text{w/c} < 0.75$), saturated concretes. Diffusion/sorption in partially saturated concrete is important in many field exposures but is not addressed in this study. However, we do allow for the presence of entrained air bubbles. In addition, we are only considering ionic diffusion under steady-state conditions, and so ignore the short time effect of chloride binding.

Microstructure Models

In this section we describe the individual microstructure models that are used to build the multiscale model. In the next section we show how these individual models are fitted together to generate the multiscale approach.

TABLE 1. Aggregate particle size distributions for various concretes

Sieve Parameters		Fraction of Aggregate Volume Contained in Sieve			
D_L (mm)	D_H (mm)	cfcc	fffc	ffcc	cffc
0.075	0.15	0	0.04	0.04	0
0.15	0.30	0.02	0.08	0.08	0.02
0.30	0.60	0.08	0.12	0.12	0.08
0.60	1.18	0.1	0.1	0.1	0.1
1.18	2.36	0.12	0.09	0.06	0.15
2.36	4.75	0.06	0.06	0	0.12
4.75	9.525	0.26	0.33	0.24	0.35
9.525	12.7	0.3	0.18	0.3	0.18
12.7	19.05	0.06	0	0.06	0

Note: cfcc = coarser fine particles, coarser coarse particles; cffc = coarser fine particles, finer coarse particles; ffcc = finer fine particles, coarser coarse particles; fffc = finer fine particles, finer coarse particles. D = particle diameter.

Concrete (millimeter scale)

For modeling concrete at the millimeter scale, the computational volume, typically 8000–27000 mm^3, is filled with hard spheres, representing aggregates, each surrounded by a constant thickness soft shell, representing the ITZ [9]. We assume that the ITZ thickness is not a function of the aggregate size, but is rather controlled by the median size of the much smaller cement particles [10]. A recent article used quantitative measurements of electrical conductivity to claim that the thickness of the ITZ becomes smaller for smaller aggregate particles [11]. This claim is discussed in Appendix A, where it is shown that the use of an approximate analytical equation for the concrete conductivity in reference [10] can erroneously give this result.

The aggregates are placed into the computational volume in order from largest to smallest in size and periodic boundaries are used. While the hard core aggregates may not overlap one another, the ITZs are free to overlap aggregates and each other in the placement process. A range of particle size distributions (PSDs) for the coarse and fine aggregates was chosen based on the recommendations found in ASTM C33 [12]. Sieve analyses of these four PSDs are shown in Table 1. The designations for the aggregate PSDs are cfcc, cffc, ffcc, and fffc. There are two (somewhat arbitrary) parts of the aggregate PSD, the fine particles and the coarse particles [12]. There are two limits of each PSD, a coarser one and a finer one, which result in four possible PSDs: cfcc = coarser fine particles, coarser coarse particles; cffc = coarser fine particles, finer coarse particles; ffcc = finer fine particles, coarser coarse particles; and fffc = finer fine particles, finer coarse particles. The sieve analyses reflect these designations, which can be seen upon inspection of Table 1. The coarse aggregate was of nominal size 4.75–12.5 mm

and the ratio of coarse to fine aggregate volume was fixed at 1.5:1.

Air voids were also introduced into some of the concretes. The air voids were considered to be equivalent to aggregate particles in terms of their effects on ionic diffusivity. They were assigned a diffusivity of 0 and an associated ITZ region like the aggregates [13]. We are assuming that the air voids were not filled with water. Concrete exposed to water for a long period of time may actually have the air voids filled with water. For this study, a fixed air void size distribution was used for all of the simulations based on a logarithmic probability density function [14]. Air voids smaller than 100 μm in diameter were not included in the model, as they are similar in size to the cement particles. Further details of the aggregate/air void systems used can be found in reference [8].

Cement Paste (micrometer scale)

The tricalcium silicate cement hydration model used in this multiscale model has been described in detail elsewhere [15,16]. The cement powder to be modeled is represented by nonoverlapping digitized spheres following the PSD measured on actual cement samples. Various PSDs can be used, although we have only examined PSDs with median particle diameters of 10, 20, and 30 μm [17]. Based on previous modeling studies [9], we take the ITZ widths equal to the median cement particle size. To minimize finite size effects, periodic boundaries are used during particle placement, such that a particle that extends outside of one face of the 3-D computational volume is completed into the opposite side of the system. For the micrometer-scale model, each pixel element represents 1 μm^3 in volume. The system sizes needed ranged from 20–30 million pixels. The cement particles are placed in order of size from largest to smallest at random locations in the 3-D microstructure such that they do not overlap each other or the aggregate particle.

After initial particle placement, a simple cellular automaton model is used to model the hydration reactions between tricalcium silicate and water [18]. In this model, cement pixels in contact with water dissolve at random, diffuse within the pore space, and react to form calcium hydroxide crystals in the pore space and calcium silicate hydrate gel (CSH) on the surfaces of the original cement particles and previously deposited CSH (C = CaO, S = SiO$_2$, H = H$_2$O). For these studies, the aggregate is considered inert and does not participate in the hydration reactions. At any degree of hydration, the porosity can be determined as a function of distance from the aggregate surface. Initially, after particle placement, the ITZ region contains a higher w/c ratio (more porosity) than the bulk paste due to the inefficient

packing of the cement particles, the so-called wall effect [19,20]. During hydration, the porosity is reduced throughout the cement paste, but still remains higher in the ITZ regions. Thus, these regions will typically have a higher diffusivity than the bulk paste regions. Once porosity has been quantified, the relative diffusivity, D/D_o, as a function of distance from the aggregate surface, x, can be estimated using a previously established relationship [21]:

$$\frac{D}{D_o}(x) = 0.001 + 0.07\phi(x)^2 + 1.8H(\phi(x) - 0.18)$$
$$\times (\phi(x) - 0.18)^2 \tag{1}$$

where relative diffusivity is defined as the ratio of the diffusivity D of ions in the material of interest relative to their value in bulk water, D_o, $\phi(x)$ is the capillary porosity volume fraction at a distance x from an aggregate surface, and H is the Heaviside function having a value of 1 when $\phi > 0.18$ and a value of 0 otherwise. This equation comes from fitting the results of several different w/c cement pastes at many different degrees of hydration, where a value of diffusivity for the C-S-H phase was used, which agrees with nanometer-scale simulations of C-S-H nanostructure and properties [5]. The constant term in eq 1 comes from the limiting value of diffusion through C-S-H gel pores, when the capillary porosity is zero, the H term represents diffusion through percolated capillary porosity, and the second term in eq 1 is a fitting term that connects the two limiting behaviors [21]. Equation 1 is not exact, of course, but should give results accurate to at least a factor of two for the absolute diffusivity, and better than that for ratios of ITZ to bulk diffusivity, for the usual range of capillary porosity encountered (10–40%). References [21,22] give experimental validation of this model and the associated eq 1, although improvements are possible.

Multiscale Model

An approach to computing the diffusivity of concrete has been previously discussed [7,23]. This involved using just the concrete microstructure model described, along with random walker techniques, to compute the ratio of the concrete diffusivity to the bulk cement paste diffusivity as a function of the ITZ diffusivity and the aggregate volume fraction. The value of diffusivity produced was relative to the value assigned to the bulk paste phase.

One might then naively think that an analogous experimental measurement would be to measure the concrete diffusivity as a function of the degree of hydration and measure the diffusivity of the cement paste from which the concrete was made (same w/c

ratio). Normalizing the concrete diffusivity by the cement paste diffusivity at the same degree of hydration would presumably then give a number that could be compared to the model number [7,23]. As was pointed out in reference [7], this approach is not entirely correct. The main reasons are the way concrete is made and the effect of the ITZ. The following example will serve to illustrate this point.

Suppose a concrete was made by mixing a 0.5 w/c cement paste with enough aggregates so that the final volume fraction of aggregates is 60%. If the ITZ is 20 μm thick, then all cement paste within this distance from an aggregate will, on average, have a higher porosity and therefore a w/c ratio higher than 0.5. This is because there is known to be less cement in the ITZ than in the bulk paste [9,19]. But the only way this can happen is for the cement paste outside the ITZ region to have a w/c ratio that is less than 0.5 and therefore a lower porosity, since the average w/c ratio has been specified to be 0.5 by the initial mixing conditions. If the ITZ volume fraction is small, then this effect is also small, which would be the case for a small aggregate volume fraction. However, as the amount of aggregate increases, the ITZ volume fraction also increases, and this effect becomes quite appreciable. So for this hypothetical concrete, it would be incorrect to consider a 0.5 w/c ratio cement paste to be the matrix or bulk phase for the concrete. The actual bulk paste, where "bulk" means outside the ITZ region, would have a lower w/c ratio, possibly as low as 0.4. Therefore, concrete is *not* a simple two-phase composite of cement paste plus aggregates, and not even a simple three-phase composite of aggregates plus ITZ and bulk cement paste. Concrete is rather an *interactive composite*, where the amount of the aggregates influences the properties and amounts of the cement paste phases. The multiscale model approach described in this article is designed to approximately take this effect into account, by combining models to actually compute this redistribution of cement and w/c ratio.

The multiscale model works in three steps. It is not a particularly simple model, as it is addressing a complex interactive composite material.

(1) The first key step is, using the millimeter-scale concrete microstructure model, to place aggregate particles, following the aggregate PSD of interest, into the concrete volume. The cement PSD is used to establish the interfacial zone thickness, t_{ITZ}. The value of t_{ITZ} is taken to be equivalent to the median cement particle diameter, ignoring any effects of bleeding [10]. Systematic point sampling is then used to determine the volume fractions of ITZ (V_{ITZ}) and bulk (V_{bulk}) paste for this particular choice of aggregate PSD and value of t_{ITZ} [9].
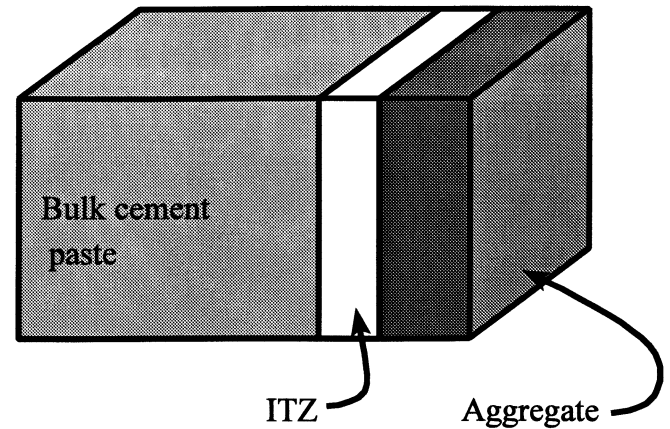
(2) The second key step uses the micrometer-scale

FIGURE 1. Breakdown, in the cement hydration computational volume, of aggregate, interfacial transition zone (ITZ) cement paste, and bulk cement paste (not to scale).

cement hydration model. The shape of the model volume is shown in Figure 1, with aggregate, ITZ, and bulk paste regions defined. We want to determine the local microstructure near a single aggregate surface, in order to be able to compute the contrast between ITZ and bulk paste diffusivities. The dimensions of the model box are chosen so as to match the ratio of V_{ITZ}/V_{bulk} (determined in step 1). By matching the ratio V_{ITZ}/V_{bulk} as determined in the concrete volume, we approximate the microstructure that exists near a typical aggregate surface.

Cement particles are placed into this computational volume, following the cement PSD, to achieve the specified total w/c ratio. Of course, the w/c ratios in the two regions will be different, because of the wall effect of the aggregate surface. The actual numerical difference is a prediction of the micrometer-scale microstructure model and is not specified by the user. The cement particles are then hydrated, using the model, up to a desired degree of hydration. After hydration, the porosity ϕ is measured as a function of distance from the aggregate surface. Using eq 1, which gives the cement paste diffusivity as a function of the capillary porosity ϕ, the diffusivity as a function of distance from the aggregate surface is computed. This diffusivity is relative to the diffusivity of ions in the pore fluid [21]. These diffusivity values are averaged in two subsets, those lying within a distance t_{ITZ} of the aggregate and those in the "bulk" paste, to give two values, D_{ITZ} and D_{bulk}. Averaging in this way assumes that the diffusive flow in the two phases is locally parallel to the aggregate surface, and so each layer can be simply summed up. By averaging over t_{ITZ}, the simplifying approximation is made that the ITZ has a fixed width with fixed properties. The average over the simulated local microstructure of the interfacial transition region is done to

help make this approximation more accurate. Choosing a different value of t_{ITZ} would of course give a different value of ITZ diffusivity. Other ways of averaging over the local microstructure are possible, such as matching to an exact solution of a single specific size aggregate with a gradient of properties around it [24]. Other methods do not, however, seem to make a significant difference in the final results [24].

After the first two steps, we now have a microstructure model of the concrete, using spherical aggregates that follow the correct PSD, and we have values of diffusivity for each of the three phases in the model concrete: aggregate ($D_{agg} = 0$), bulk cement paste (D_{bulk}), and ITZ cement paste (D_{ITZ}). It is crucial to remember that the values of D_{bulk} and D_{ITZ} were determined interactively, since the amount and size of the aggregates was used to determine the value of V_{ITZ}/V_{bulk} that was used in the cement paste model, which in turn helped determine the value of D_{ITZ}/D_{bulk}. In principle the ratio of D_{ITZ}/D_{bulk} is a function of the aggregate PSD and volume fraction and the degree of hydration.

(3) The third key step is to finally use the ratio of the bulk and ITZ cement paste diffusivities, D_{ITZ}/D_{bulk}, as an input back into the original concrete model [7,23]. Random walk numerical techniques are then used to compute the diffusivity of the overall concrete system. The random walker techniques used for this calculation have been previously described [7,23]. These techniques are quite computer-time intensive, but do not use huge amounts of memory. The relative diffusivity of the concrete, D_{conc}/D_{bulk}, is calculated by this algorithm [6,7,23]. This value can then be converted into an absolute chloride ion diffusivity for the concrete, D_{conc}, by multiplying it by D_{bulk}/D_o determined from the cement-level microstructural model [eq 1] and by D_o, the diffusion coefficient of chloride ions in bulk water at room temperature, given as $2.0 \cdot 10^{-9}$ m^2/s [25]. By changing the value of D_o to correspond to that measured for the specific ion of interest, the techniques can be generalized to other ionic species of relevance in cement-based materials. This model does not address chemical effects such as binding and reactions.

Analytical Methods

The main point of this article is to show how the first and third key steps, as described, can be accurately replaced by analytical equations. This will aid in further applications of the multiscale model to other concrete mixtures, by making the multiscale model usable by those without access to large amounts of computing power. This replacement will also make the model easier to use for parameter studies, as run times for the

random walker step, step (3), can take weeks of clock time.

Interfacial Zone Volume: Step (1)

An analytical estimate for the total interfacial zone volume around a collection of spheres of various sizes can be obtained from the literature on the statistical geometry of composites [26]. In this work, a collection of spheres of various sizes are randomly placed in a volume according to *equilibrium* statistics. These involve treating the spheres as being dispersed in a liquid, where the effect of gravity is neglected, and allowing them to be "shook" sufficiently so as to achieve their desired positions. This process is actually similar to how a real concrete is mixed. In the case of our concrete model, however, the particles are placed according to nonequilibrium random parking statistics [27], as described. Notably, the equilibrium and the random parking statistics are essentially identical for single-size spheres up to about 20% volume fraction of spheres.

It would seem that this analytical estimate could not be applied to our model, which has randomly parked aggregates. However, we were encouraged to do so by results we obtained for monosize spheres, randomly parked at 27% by volume [28]. Monosize spheres are the worst case, where the most differences can be seen between random parking and equilibrium distributions. However, the Lu and Torquato analysis worked very well even for this system, so we have applied it as well to these concrete systems. Why this should be is not known at present, but is the focus of further research.

There are many analytical results contained in the article by Lu and Torquato [26] that are relevant to the concrete problem. In this article we focus on the quantity $e_V(r)$, the "void exclusion probability" as denoted in reference [26] (note: in our case, "void" means outside the aggregates). As formulated by Lu and Torquato, if one adds a spherical shell of thickness r around each one of the spherical particles, then the volume fraction of material outside of both the particles and the shells is just $e_V(r)$. The ITZ volume fraction, V_{ITZ}, is then just:

$$V_{ITZ} = 1 - e_V(t_{ITZ}) - \eta \tag{2}$$

where η is the volume fraction of aggregates [26]. The functional form of $e_V(r)$ is:

$$e_V(r) = (1 - \eta)\exp[-\pi\rho(cr + dr^2 + gr^3)] \tag{3}$$

where ρ is the total *number* of aggregates per unit volume, and the coefficients c, d, and g are given in terms of averages ($\langle \ldots \rangle$) over the PSD of the aggregates in terms of *number*, not volume. These averages can be determined from the sieve analysis, using certain

TABLE 2. Parameters of model systems used, including point-counting result for V_{ITZ} and random walker results for D/D_{bulk}

System	V_{agg}	V_{air}	PSD	t_{ITZ}(mm)	D_{ITZ}/D_{bulk}	V_{ITZ}	D/D_{bulk}
1	0.599	0	cfcc	0.03	2.24	0.0580	0.34
2	0.757	0	cfcc	0.01	4.94	0.0208	0.23
3	0.754	0	fffc	0.03	2.54	0.1647	0.28
4	0.601	0	cffc	0.03	4.22	0.0595	0.42
5	0.594	0	fffc	0.01	5.00	0.0431	0.42
6	0.757	0.0948	cfcc	0.03	4.48	0.1167	0.30
7	0.753	0	cffc	0.01	2.95	0.0242	0.20
8	0.752	0	ffcc	0.03	3.31	0.1577	0.34
9	0.601	0.0948	cffc	0.01	2.15	0.0422	0.25
10	0.602	0	ffcc	0.01	2.84	0.0458	0.36
11	0.752	0.0825	ffcc	0.01	2.34	0.0655	0.16
12	0.754	0.0775	fffc	0.01	1.18	0.0744	0.11
13	0.599	0.0948	cfcc	0.01	1.26	0.0421	0.22
14	0.594	0.0948	fffc	0.03	5.34	0.2008	0.69
15	0.753	0.0948	cffc	0.03	7.24	0.1214	0.47
16	0.602	0.0948	ffcc	0.03	8.34	0.2029	1.05
17	0.524	0	cfcc	0.01	4.06	0.0164	0.42
18	0.824	0	cfcc	0.01	4.14	0.0231	0.16
19	0.675	0	cfcc	0.01	2.32	0.0190	0.26
20	0.675	0	cfcc	0.01	7.53	0.0190	0.33
21	0.675	0	cfcc	0.01	1.08	0.0190	0.23
22	0.675	0	cfcc	0.01	1.88	0.0190	0.24

Note: PSD = particle size distribution; cfcc = coarser fine particles, coarser coarse particles; cffc = coarser fine particles, finer coarse particles; ffcc = finer fine particles, coarser coarse particles; fffc = finer fine particles, finer coarse particles. D = particle diameter.

reasonable assumptions, as shown in Appendix B. The coefficients c, d, and g are:

$$c = \frac{4\langle R^2\rangle}{1 - \eta} \tag{4}$$

$$d = \frac{4\langle R\rangle}{1 - \eta} + \frac{12\epsilon_2\langle R^2\rangle}{(1 - \eta)^2} \tag{5}$$

$$g = \frac{4}{3(1 - \eta)} + \frac{8\epsilon_2\langle R\rangle}{(1 - \eta)^2} + \frac{16A\epsilon_2^2\langle R^2\rangle}{3(1 - \eta)^3} \tag{6}$$

where $\epsilon_2 = 2\pi\rho\langle R^2\rangle/3$, and A is a parameter that can have different values (0, 2, or 3) depending on the analytical approximation chosen in the theory [26]. The actual choice used may be fixed by experiment. In all the work on concrete, the actual value of A used did not make much difference, but $A = 0$ was always slightly better than $A = 2$ or 3, as judged by comparison to the exact (numerical) values listed in Table 2. Note that there is a misprint in eq 4.27 in Lu and Torquato [26], which is corrected in the present eqs 4–6.

It should be noted that eqs 2 and 3 can be used to map out the volume fraction of cement paste that is within a distance r of an aggregate surface. The accuracy of eq 2, as will be demonstrated, might very well allow it to be used to help theoretically analyze a phenomenon like alkali-silica reaction, where cement paste constituents, namely alkalis in the pore solution [29], must diffuse to an aggregate surface in order for the alkali-silica reaction to take place. Another possibility might be the reactivity of calcium hydroxide with fly ash, where calcium from the calcium hydroxide particle must diffuse to the silica-rich fly ash, because of the higher mobility of calcium in solution compared to silica. The distance of the cement paste to the nearest aggregate surface or of a calcium hydroxide crystal to the nearest fly ash particle then must obviously be important for the kinetics of these processes.

Differential Effective Medium Theory

Most kinds of "effective medium theories" for two or more phase composites are derived in two steps. In the first step, the dilute limit of the composite, where the inclusion phases are present in small amounts in the matrix material, is solved exactly. The second step takes this exact solution for the dilute limit and uses a statistical approximation of some kind to get an analytical form for the case of arbitrary amounts of the phases.

The type of effective medium theory (EMT) that we have found useful for this kind of conductivity problem uses the differential scheme to generate the EMT, hereafter referred to as D-EMT. The mathematical basics are found in McLaughlin [30] and have been previously discussed in the context of concrete [23]. The first step in generating the D-EMT equation is to solve

the dilute limit properly. In this case, the dilute limit is given by a single spherical aggregate particle, with $D_{agg} = 0$, surrounded by a spherical shell of thickness t_{ITZ}, of diffusivity D_{ITZ}, embedded in a matrix with diffusivity D_{bulk}. Diffusivity or electrical conductivity can be used interchangeably for this problem, as the mathematical structure is identical. If there is a very low volume fraction of such particles, then the diffusivity of the composite is described by the expansion:

$$\frac{D}{D_{bulk}} = 1 + \langle m \rangle_V c + O(c^2) \tag{7}$$

where $\langle m \rangle_V$ means that the slope is averaged over the *volume* distribution of the aggregates, since the expansion eq 7 is in terms of the aggregate volume fraction, not the number fraction. The slope m for a single-size particle is given in Appendix A.

To generate the D-EMT equation, the dilute result is used in the following way. Suppose that a volume fraction c' of aggregate has been added to the cement paste matrix, so that the total diffusivity is now D'. The current matrix volume fraction is $\phi' = 1 - c'$. We have "smeared" out the aggregates so that the concrete is a uniform material. Suppose that a differential volume element of volume fraction dV is now taken out and replaced with aggregate. The new actual volume fraction of aggregate is not just $c' + dV$, since some of the material that was removed was also aggregate, but is equal to $c' + dV - c'dV$. The change in aggregate volume fraction is then just $dc' = dV(1 - c')$. The dilute limit is used to get the new diffusivity $D' + dD'$ (eq 8):

$$D' + dD' = D' + D'\langle m \rangle dV \tag{8}$$

or, using the relation between c' and dV:

$$\frac{dD'}{D'\langle m \rangle_V} = \frac{dc'}{1 - c'}. \tag{9}$$

Equation 9 can be integrated on the left from D_{bulk}, the diffusivity when no aggregates are present, to D, the diffusivity when the aggregates have volume fraction c, and on the right from 0 to the desired aggregate volume fraction c, with the final result:

$$-\int_{D_{bulk}}^{D} \frac{dD'}{D'\langle m \rangle_V} = ln(1 - c). \tag{10}$$

In eq 10, D_{bulk} has been replaced by D' in the expression for $\langle m \rangle_V$ (see Appendix A). To obtain the predicted value of D for any value, c, of aggregate volume fraction, one simply varies the value of D until the left-hand integral equals the desired value of $ln(1 - c)$.

There is one complication of this three-phase model, compared to two-phase models [30]. In two-phase models, in the D-EMT process, the diffusivity of the inclusion would remain invariant, while only the matrix diffusivity would change. In this three-phase case, there is the question of whether the ITZ diffusivity, D_{ITZ}, is also renormalized in the D-EMT process, or whether it should stay invariant. The ITZ phase is outside the aggregate volume, and so must be considered part of the matrix phase. Intuitively and physically, there are two extremes that are worth considering. One is that the actual value of D_{ITZ} remains invariant. The other is that the value of D_{ITZ}/D' remains constant at what the original value, D_{ITZ}/D_{bulk}, was chosen to be. If the concrete diffusivity is being reduced with the addition of aggregates, then the first choice will clearly give a larger result. If the overall concrete diffusivity is going up with the addition of more aggregate, then the second will clearly give the larger value. Theoretically, it is not possible to choose between these ways of carrying out the D-EMT process, as the value of D_{ITZ} is essentially a free parameter when solving the D-EMT problem for $c > 0$. In the next section, we will show how the numerically exact random walker calculations of D/D_{bulk} can show us how to make a choice between these two limits.

Results

Table 2 lists the numerical point counting and random walker results for the interfacial zone volume fraction and D/D_{bulk}, respectively, for 22 systems studied previously [8]. The parameters listed are enough, along with the sieve data in Table 1, to allow the analytical equations listed previously to be used to calculate the interfacial zone volume and the value of D/D_{bulk}.

Figure 2 shows the ITZ volume fraction, calculated from eq 2, plotted against the exact numerical ITZ volume fraction as given by point counting. Equation 2 is evaluated for $r = t_{ITZ}$, the interfacial zone width. Clearly there is excellent agreement, within a few percent, over a large range of ITZ volume fractions. At the low volume fractions, there is very little overlap of the interfacial zones, so that an accurate prediction of the total ITZ volume can be made simply by adding up the interfacial zone volume of each aggregate particle and assuming there is no overlap. Equation 2 does correctly reduce to this limit and so still works well. In the higher volume fractions in Figure 2, there is substantial ITZ overlap, and so the close agreement of eq 2 with the numerical results is even more impressive. Further investigations of this equation applied to concrete models can be found elsewhere [28].

Figure 3 shows the D-EMT result for D/D_{bulk} plotted against the random walker numerical result. The
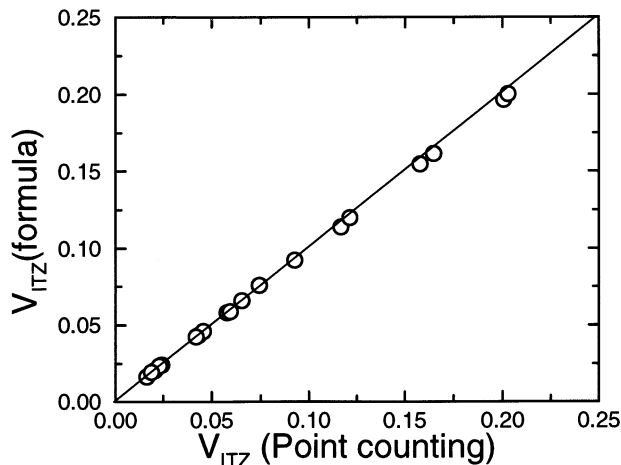
FIGURE 2. Interfacial transition zone (ITZ) volume fraction, as computed by eq 2, plotted against the exact (numerical) results of point counting, for each of the 22 concretes listed in Table 2 [6]. The abscissa values are given in Table 2. The solid line is the line of equality.

D-EMT result takes a weighted average of the two possible choices for solving the D-EMT equation, as discussed in the previous section. If choice number one is that of fixing the value of D_{ITZ}, resulting in the value D_1/D_{bulk}, and choice number two is fixing the value of D_{ITZ}/D_{bulk}, resulting in the value D_2/D_{bulk}, then the average used is:

$$\frac{D_{EMT}}{D_{bulk}} = 0.78D_1 + 0.22D_2. \tag{11}$$

The dashed lines in Figure 3 correspond to the line of equality and the ±20% error boundaries. All the D-EMT
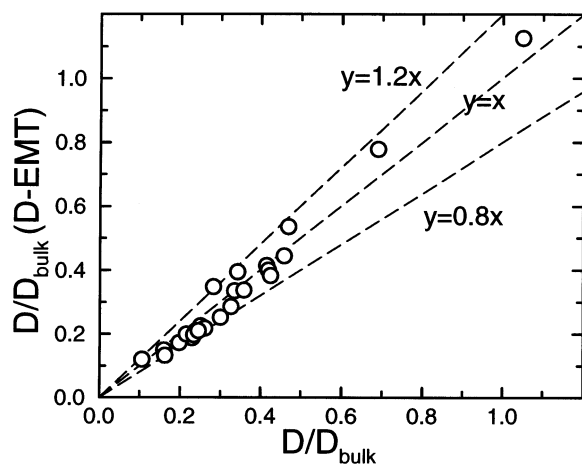

FIGURE 3. D-EMT value of D/D_{bulk}, plotted against the exact (numerical) myopic walker results, listed in Table 2. The dashed lines consist of the line of equality, bracketed by lines of ±20% error.

results, using eq 11, stay within the ±20% lines, and most stay well within. This choice of weighting of these two extremes agrees well with the results of direct simulation for a wide range of concretes and is expected to be quite robust and apply to other concretes as well. Choosing a weighted average is the mathematical analogy of saying that in a real concrete, the interfacial zone diffusivity becomes partially blended in with the rest of the matrix phase due to the action of nearby aggregates.

We note that, a priori, there is no reason to expect an EMT to work well for a particular problem. The dilute limit used in the development of an EMT is exact, but the approximation used to produce predictions for larger volume fractions of aggregate is essentially uncontrolled. Having numerically exact diffusivity calculations available makes it possible for us to quantitatively evaluate the D-EMT predictions and optimize them for practical use. The D-EMT results can now be used to replace the random walker numerical results, but the validity of this replacement could only have been determined by having the random walker techniques available in the first place.

Discussion

It has been shown that two fairly simple analytical formulas can give a quite accurate description of numerical results on a wide range of concrete mixtures. These formulas must be evaluated numerically, using numerical quadrature techniques like Gaussian integration, but these kind of integration techniques are easily available. The numerial integrations can easily be done on a workstation or a fast personal computer. Therefore, the supercomputer simulations inherent in two of the three key steps in the multiscale model of concrete diffusivity can be replaced with simple analytical formulations. It is also encouraging to note that the second key step, that of numerically hydrating cement grains around an aggregate, is the easiest step computationally, since it uses only integers. The system sizes used in this article and in reference [8] were of the order $30 \cdot 10^6$ pixels. For the hydration code necessary for this model, only one byte per pixel is needed to keep track of the phases before, during, and after hydration, so that approximately 30 MB of memory are needed for this part of the multiscale model. This much memory is even becoming common for modern personal computers and has long been common for low-end engineering workstations, so that even without an analytical replacement, this part of the model should be accessible to many concrete designers, at least in principle. Of course, run times on a personal computer will be slow, on the order of probably tens of hours, but quite faster on low-end workstations.

The largest difference between this multiscale model

and previous work [7,23], as was mentioned in the Introduction, is the ability to take into account, even in an approximate way, the redistribution of cement due to the presence of the aggregates. This gives more accurate values of D_{ITZ} and D_{bulk}. This step appears to be crucial, especially at the high volume fractions of aggregate common in concrete, as this redistribution of cement plays an important role in determining the bulk properties of the concrete. The procedure used in the multiscale model to determine this ratio, step (2), is still approximate, since the gradient of properties in the interfacial zone is treated as being equivalent to a fixed width, fixed property interfacial zone surrounded by fixed property bulk cement paste. This matching of gradient to interfacial zone can be done more accurately and has been the subject of further research [24]. It turns out that the end results are not significantly affected [24].

One consequence of this cement redistribution is a sort of "negative feed-back" loop, in the following sense. Suppose the ITZ is made wider, perhaps by using a coarser cement. This would tend to drive up the value of D_{ITZ} and lower the value of D_{bulk}, so that the ratio of the two is larger, implying a larger value of D/D_{bulk} [7]. However, the actual value of D will not be as much higher as one would think, since the higher value of D/D_{bulk} must be multiplied by the lower value of D_{bulk} to get the overall concrete diffusivity. So just increasing the diffusivity of the interfacial zone by thickening it will not increase the overall concrete diffusivity as much as one would think [8]. Increasing the surface area of the aggregate by reducing the average aggregate diameter results in similar behavior. Other interplays between the variables of the problem are discussed in reference [8].

The proper experimental validation of the multiscale model remains to be done. In order to be able to use the model to compare with experimental results, one cannot just prepare concretes at various aggregate volume fractions, including the zero volume fraction of aggregate cement paste matrix, and then simply normalize the concrete measurements by cement paste measurements taken at equal times. The redistribution of cement in the concrete makes the value of D_{bulk} in the concrete not the same as the plain cement paste sample, even at equal degrees of hydration.

What must be done experimentally is the following. The degree of hydration of the concrete must be determined, along with the volume fraction and particle size distribution of the aggregates, and the particle size distribution of the cement, or at the very least its median particle size. The diffusivity or electrical conductivity of the concrete can then be measured. If the experimental measurements are taken in this manner, then the model can be quantitatively tested and im-

proved, making it a useful tool for designing the ionic diffusivity of concrete at the mix design stage. This procedure is now being carried out for mortars with various amounts of sand, and results will be reported in the near future [31].

Summary

This article has described a multiscale model for predicting concrete diffusivity based on the amounts and sizes of the concrete components. This model has three key steps, using: (1) a millimeter-scale concrete microstructure model; (2) a micrometer-scale cement paste microstructure model; and (3) a diffusivity calculation of the concrete microstructure model. The two main results of this article are that the large computer simulations that were previously necessary for steps (1) and (3) can now be accurately replaced with simple analytical equations, making the multiscale model easier and faster to use.

Appendix A

Discussion of Dependence of ITZ Thickness on Aggregate Size

In reference [9], it was found that the ITZ thickness decreased with aggregate radius, in contradiction to our assumption that the ITZ thickness is independent of aggregate size, at least for aggregates larger than a few times the median cement particle size. This conclusion in reference [9] was reached by making electrical conductivity measurements, equating the data to an equation for the composite conductivity that had as parameters the aggregate volume fraction, the thickness and conductivity of the interfacial zone, the bulk paste conductivity, and the average radius of the aggregates, taken to be spheres. The value of the interfacial zone thickness, normalized to some arbitrary value, was then found from this matching process. The trouble with this procedure is, as will be shown below, that the equation used was only an approximate one. Its dependence on the interfacial zone thickness, for example, is only approximate and so will not give correct results in the above procedure.

A simple test is in the dilute limit, where the diffusivity is known exactly. In this limit, as was discussed in the text, the diffusivity, normalized by the bulk diffusivity, is (eq A.1):

$$\frac{D}{D_{bulk}} = 1 + mc \tag{A.1}$$

where c is the volume fraction of aggregates placed. The exact result for m, for a spherical aggregate of radius r, with zero aggregate diffusivity, is:

$$m = (3\beta)\, \frac{2(\beta - 1)\, \dfrac{D_{ITZ}}{D_{bulk}} - (1 + 2\beta)}{2(\beta - 1)\, \dfrac{D_{ITZ}}{D_{bulk}} + 2(1 + 2\beta)} \qquad (A.2)$$

where the parameter $\beta = [(r + t_{ITZ})/r]^3$ contains all of the dependence on the particle and interfacial zone dimensions [7]. (There is a typographical error in reference [7], in the equation equivalent to eq A.2. In the numerator, the term that reads $(b + h)/h$ should really be $(b + h)/b$, in accordance with the definition of the parameter β).

The equivalent value for m, derived from the equation in reference [8], with $s = D_{ITZ}/D_{bulk}$, is:

$$m_{eff} = -\frac{3}{2} + 3(s - 1)\, \frac{t_{ITZ}}{r} + \frac{3}{2}(s - 1)\left(\frac{t_{ITZ}}{r}\right)^2 \qquad (A.3)$$

where r is the aggregate radius. All the aggregate must be of the same size for this equation to apply to a concrete. In eq A.2, if we treat t_{ITZ}/r as a small parameter, and expand the exact result of eq A.2 to second order in this parameter, then the following equation results:

$$m_{eff} = -\frac{3}{2} + \frac{9}{2}(s - 1)\, \frac{t_{ITZ}}{r} - \frac{9}{2}(s - 1)\left(\frac{t_{ITZ}}{r}\right)^2. \qquad (A.4)$$

Comparison of eq A.3 to eq A.4 shows that only the $-3/2$ term agrees. So eq A.3 is not correct, in the dilute limit, in either the first or the second order term in t_{ITZ}/r.

If we set eq A.3 equal to eq A.2, simulating the matching of eq A.3 to an "experimental" result, then we can solve for the "effective" value of t_{ITZ}/r needed in order to match up eq A.3 to the correct value of eq A.2. This equation (eq A.5) is:

$$(t_{ITZ}/r)_{eff} = -1 + \left[\frac{3s + 2m}{3(s - 1)}\right]^{1/2} \qquad (A.5)$$

where m is the exact slope from eq A.2. In this way, we can generate a graph of the perceived value of t_{ITZ} measured as a function of the particle radius, in a case where the actual value of t_{ITZ} is fixed. We take $t_{ITZ} = 20$ μm, and the ratio s of the ITZ diffusivity to the bulk diffusivity to be 4 and 10. Figure 4 shows the results of this process. Clearly, using the equation from reference [9], the ITZ thickness is perceived to be sharply decreasing with particle radius, when in fact it is staying constant, as indicated by the horizontal line. Even though the measurements in reference [9] were made at aggregate volume fractions well beyond the dilute
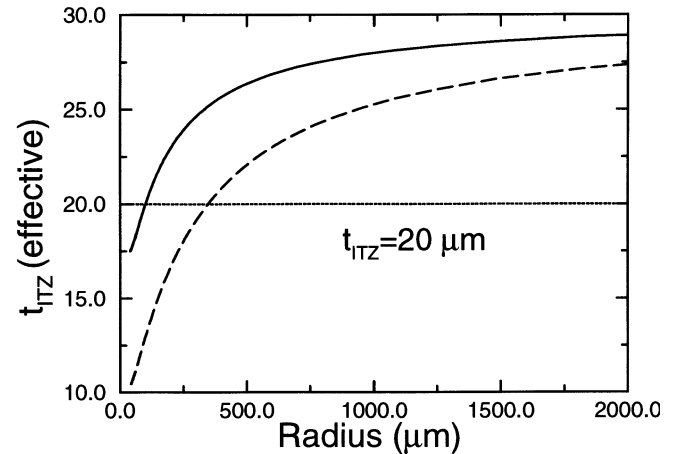

FIGURE 4. "Effective" value of t_{ITZ}/r, as determined from matching the approximate formula of eq A.3 to the exact formula of eq A.2 (see eq A.5), plotted against the radius of the aggregate particle r, for two different values of $s = D_{ITZ}/D_{bulk}$ (solid line $s = 4$, dashed line $s = 10$).

limit, the same result will almost certainly hold. Therefore, the conclusion of reference [9] that the ITZ thickness decreases with aggregate radius was based on a formula that was not correct in accounting for the effect of the ITZ, and so when used to "back out" a value for D_{ITZ}/D_{bulk}, gave incorrect results. This would be the case even if eq A.3 gave reasonable results for m for a concrete, since the specific dependence on D_{ITZ}/D_{bulk} is not correct. The error occurs when trying to extract a small quantity out of an experimental measurement using an inexact equation that does not have the correct dependence on the small quantity, in this case the ITZ thickness.

Appendix B

Using a Sieve Analysis to Compute Statistical Quantities Needed

A typical sieve analysis of an aggregate can be expressed in terms of d_i, M, and c_i, where c_i is the fraction of the total volume of aggregate that has a diameter between d_i and d_{i+1}, $d_i < d_{i+1}$, and M is the total number of sieves used. The units of the particle diameters are millimeters. The sum of c_i over the M sieves = 1. A typical sieve analysis is expressed in terms of the mass fraction passing or retained by a certain sieve size, which can easily be converted to the form given here. If aggregates of different size have all the same density, then mass fractions are the same as volume fractions.

Now, in the ITZ volume formulas, averages appear of powers of the aggregate radii, averaged over the number distribution density of the aggregates. Here we show how this can be carried out using the sieve

analysis, followed by formulas for performing volume averages using the sieve analysis, which is necessary to be able to evaluate the D-EMT formulas for a given aggregate PSD.

In order to carry out these averages, we need to make an assumption as to how the aggregates are distributed within each sieve. That information is not given by a sieve analysis. Many assumptions are possible, but two that are easy to handle analytically, and are physically reasonable, are that either the aggregates are distributed, within a sieve, uniformly by volume or uniformly by diameter. We show the analysis for both assumptions, although in all the simulation work, the former assumption was used. We could, of course, also assume that all the aggregates in a sieve have the same radius, perhaps equal to the average of the endpoints of the sieve range, but it is probably more accurate to assume some kind of distribution within the sieve.

ASSUMPTION 1: UNIFORM DISTRIBUTION BY VOLUME. In this case, the fraction of the total aggregate volume represented by particles with volumes in the range $(V, V + dV)$, contained in the ith sieve, is given by:

$$p(V)dV = \frac{c_i dV}{(V_{i+1} - V_i)} \tag{B.1}$$

so that the integral over the interval (V_i, V_{i+1}) will be equal to c_i. If N is the total number of aggregate particles used per the total concrete volume V_{TOT}, so that $\rho \equiv N/V_{TOT}$, V_{agg} is the total aggregate volume, $c_{agg} = V_{agg}/V_{TOT}$, then the fraction of the total *number* of aggregate particles with volumes in the range $(V, V + dV)$, contained in the ith sieve, is given by (eq B.2):

$$n(V)dV = \frac{c_{agg} c_i dV}{\rho V(V_{i+1} - V_i)} \tag{B.2}$$

where V is the volume of a particle in this range. If we now convert to radius, using $V = 4\pi r^3/3$ and $dV = 4\pi r^2 dr$, the equivalent expression in terms of the particle radius is:

$$n(r)dr = \frac{9 c_{agg} c_i r^{-1} dr}{4\pi \rho(r_{i+1}^3 - r_i^3)}. \tag{B.3}$$

Integrating over each sieve's endpoints and summing over each sieve must give 1 for this expression:

$$1 = \sum_{i=1}^{M} \int_{r_i}^{r_{i+1}} n(r)dr. \tag{B.4}$$

This normalization determines the value of ρ (eq B.5):

$$\rho = \sum_{i=1}^{M} \frac{9 c_{agg} c_i}{4\pi(r_{i+1}^3 - r_i^3)} \ln\left(\frac{r_{i+1}}{r_i}\right). \tag{B.5}$$

Therefore, the average of R^n over the particle number density, as shown in eq B.3, is then (eq B.6):

$$\langle R^n \rangle = \sum_{i=1}^{M} \frac{9 c_{agg} c_i}{4\pi \rho(r_{i+1}^3 - r_i^3)} \int_{r_i}^{r_{i+1}} r^{n-1} dr. \tag{B.6}$$

ASSUMPTION 2: UNIFORM DISTRIBUTION BY RADIUS. In this case, the fraction of the aggregate volume represented by particles with radii in the range $(r, r + dr)$, contained in the ith sieve, is given by:

$$p(r)dr = \frac{c_i dr}{(r_{i+1} - r_i)} \tag{B.7}$$

so that the integral of $p(r)dr$ over the interval (r_i, r_{i+1}) will be equal to c_i. Similar to the previous case, the fraction of the total *number* of aggregate particles with radii in the range $(r, r + dr)$, contained in the ith sieve, is given by:

$$n(r)dr = \frac{3 c_{agg} c_i dr}{\rho 4\pi r^3(r_{i+1} - r_i)} \tag{B.8}$$

where $V = 4\pi r^3/3$ is the volume of a (spherical) particle in this range. Equation B.8 must obey the normalization eq B.4, implying that the value of ρ is then (eqs B.9 and B.10):

$$\rho = \sum_{i=1}^{M} \int_{r_i}^{r_{i+1}} \frac{3 c_{agg} c_i r^{-3} dr}{4\pi(r_{i+1} - r_i)} \tag{B.9}$$

or

$$\rho = \sum_{i=1}^{M} \frac{3 c_{agg} c_i(r_i + r_{i+1})}{8\pi(r_i r_{i+1})^2}. \tag{B.10}$$

Therefore, the average of R^n over the particle number density is (eq B.11):

$$\langle R^n \rangle = \sum_{i=1}^{M} \frac{3 c_{agg} c_i}{4\pi \rho(r_{i+1} - r_i)} \int_{r_i}^{r_{i+1}} r^{n-3} dr. \tag{B.11}$$

AVERAGES OVER THE VOLUME DISTRIBUTION. For averages over the volume distribution of the particles, either assumption can again be used. The starting points are the same for each assumption. Assuming a uniform distribution by volume within a sieve of the particles, the volume average $\langle \ldots \rangle_V$ is (eq B.12):

$$\langle f(r) \rangle_V = \sum_{i=1}^{M} \frac{3 c_i}{(r_{i+1}^3 - r_i^3)} \int_{r_i}^{r_{i+1}} r^2 f(r) dr \tag{B.12}$$

which uses eq B.1, but with $V = 4\pi r^3/3$ and $dV = 4\pi r^2$. The equation for the assumption of a uniform distribution, within a sieve, of the particles by radius, is (eq B.13):

$$\langle f(r)\rangle_V = \sum_{i=1}^{M} \frac{c_i}{(r_{i+1} - r_i)} \int_{r_i}^{r_{i+1}} f(r)dr \qquad (B.13)$$

which uses eq B.7.

Acknowledgments

References

1. Clifton, J.R.; Knab, L.I. NISTIR 89-4086, U.S. Department of Commerce, 1989.
2. Kropp, J.; Hilsdorf, H.K.; Eds. *Performance Criteria for Concrete Durability: RILEM Report 12*, E & FN Spon; London, 1995.
3. Hooton, R.D. *Cem. Concr. Aggreg.* **1995,** *17*, U1–U2.
4. Martys, N.S.; Ferraris, C.F. *Cem. Concr. Res.* **1997,** *27*, 747–760.
5. Bentz, D.P.; Quenard, D.A.; Baroghel-Bouny, V.; Garboczi, E.J.; Jennings, H.M. *Mater. Struct.* **1995,** *28*, 450–458.
6. Bentz, D.P.; Detwiler, R.J.; Garboczi, E.J.; Halamickova, P.; Schwartz, L.M. In *Chloride Penetration into Concrete*; Nilsson, L.O.; Ollivier, J.P., Eds.; RILEM, 1997.
7. Garboczi, E.J.; Schwartz, L.M.; Bentz, D.P. *Adv. Cem. Based Mater.* **1995,** *2*, 169–181.
8. Bentz, D.P.; Garboczi, E.J.; Lagergren, E.S. *ASTM Cement, Concrete, and Aggregates* **1998**: In Press. Also available at: http://ciks.cbt.nist.gov/garboczi/, Chapter 7 Section 3.
9. Winslow, D.N.; Cohen, M.D.; Bentz, D.P.; Snyder, K.A.; Garboczi, E.J. *Cem. Concr. Res.* **1994,** *24*, 25–37.
10. Bentz, D.P.; Garboczi, E.J.; Stutzman, P.E. In *Interfaces in Cementitious Composites*; Maso, J.C., Ed.; **1992,** *18*, 107–116. Also available at: http://ciks.cbt.nist.gov/garboczi/, Chapter 6, Section 3.
11. Ping, X.; Beaudoin, J.J.; Brousseau, R., *Cem. Concr. Res.* **1991,** *21*, 999–1005.
12. *Annual Book of ASTM Standards, Vol. 04.02. Concrete and Aggregates*; ASTM: Philadelphia, PA.
13. Rashed, A.I.; Williamson, R.B. *J. Mater. Res.* **1991,** *6*, 2004–2012.
14. Snyder, K.A.; Clifton, J.R. In *Proceedings of the International Conference on Building Materials: Volume 1*, Weimar, Germany, **1994**; pp. 155–158.
15. Bentz, D.P.; Garboczi, E.J. NISTIR 4746, U.S. Department of Commerce, 1992. Newest version of manual available at: http://ciks.cbt.nist.gov/garboczi/, Appendix 2.
16. Bentz, D.P.; Garboczi, E.J. *Cem. Concr. Res.* **1991,** *21*, 325–344.
17. Van Breugel, K. *Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials*, Ph.D. Thesis. Delft University of Technology: Delft, The Netherlands, **1991**;p 228.
18. Bentz, D.P.; Coveney, P.; Garboczi, E.J.; Kleyn, M.; Stutzman, P.E. *Model. Simul. Mater. Sci. Engin.* **1994,** *2*, 783–808.
19. Scrivener, K.L. In *Materials Science of Concrete, I*; Skalny, J., Ed; American Ceramic Society: Westerville, OH, 1989; pp 127–161.
20. Garboczi, E.J.; Bentz, D.P. *J. Mater. Res.* **1991,** *6*, 196–208.
21. Garboczi, E.J.; Bentz, D.P. *J. Mater. Sci.* **1992,** *27*, 2083–2092.
22. Christensen, B.J.; Mason, T.O.; Jennings, H.M.; Bentz, D.P.; Garboczi, E.J. In *Advanced Cementitious Systems: Mechanisms and Properties, Vol. 245*; Glasser, F.P.; McCarthy, G.J.; Young, J.F.; Mason, T.O.; Pratt, P.L. Eds; Materials Research Society: Pittsburgh, PA, 1992, pp 259–264.
23. Schwartz, L.M.; Garboczi, E.J.; Bentz, D.P. *J. Appl. Phys.* **1995,** *78*, 5898–5908.
24. Garboczi, E.J.; Bentz, D.P. In *Materials for the New Millenium*; Chong, K.P., Ed; ASCE: New York, 1996, pp 1228–1237. Also available at: http://ciks.cbt.nist.gov/garboczi/, Chapter 7, Section 7.
25. Mills, R.; Lobo, V.M.M. *Self-Diffusion in Electrolyte Solutions*; Amsterdam: Elsevier, 1989.
26. Lu, B.; Torquato, S. *Phys. Rev. A* **1992,** *45*, 5530–5544.
27. Cooper, D.W. *Phys. Rev. A* **1988,** *38*, 522–524.
28. Garboczi, E.J.; Bentz, D.P. *Adv. Cem. Based Mater.* **1997,** *6*, 99–108.
29. Mehta, P.K.; Monteiro, P.J.M. *Concrete: Structure, Properties, and Materials, Second Edition*. Prentice-Hall: Englewood Cliffs, NJ, 1993.
30. McLaughlin, R. *Int. J. Eng. Sci.* **1977,** *15*, 237–244.
31. Shane, J.; Mason, T.O.; Bentz, D.P.; Garboczi, E.J. Unpublished manuscript.