

Multi-Scale Microstructural Modeling to Predict Chloride Ion Diffusivity for High Performance Concrete

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MULTI-SCALE MICROSTRUCTURAL MODELING TO PREDICT CHLORIDE ION DIFFUSIVITY FOR HIGH PERFORMANCE CONCRETE

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ABSTRACT

As durability issues become increasingly prominent in concrete design, the need to predict the transport properties of a given concrete mixture becomes critical. For many degradation scenarios (corrosion, sulfate attack, etc.), the diffusion coefficient of the concrete is a critical parameter that helps determine its service life. The goal of current research at the National Institute of Standards and Technology is to develop predictive equations for the chloride ion diffusivity of concrete based on mixture proportions and expected degree of hydration. The basis for these predictions is a set of multi-scale computer-based microstructural models for cement-based materials. Modeling at the scale of micrometers (cement paste) provides the necessary information on the effects of water-to-cement (w/c) ratio, silica fume addition, and degree of hydration on the volume of capillary porosity, and its connectivity. Modeling at the scale of centimeters (concrete) provides information on the influence of volume fraction and gradation of aggregates, and interfacial transition zone (ITZ) microstructure on the effective diffusivity of the concrete composite. Connecting the models at these two scales allows for the quantitative estimation of the chloride ion diffusivity of a specific concrete. Based on the results of these models, the addition of silica fume is seen to be a very efficient means for reducing concrete diffusivity, particularly for low w/c ratio (< 0.4) systems.

INTRODUCTION

In recent years, the design of concrete structures is experiencing a paradigm shift away from strength-based criteria towards durability-based design. Additionally, there is an increasing emphasis on the application of life cycle costing techniques to evaluate the costs (and savings) of a concrete structure over the course of its lifetime. Within the Partnership for High Performance Concrete Technology (PHPCT) program at the National Institute of Standards and Technology (NIST), research is being conducted to support the development of a computer integrated knowledge

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system (CIKS) encompassing materials selection, design, quality assurance, performance prediction, and life-cycle costing of high performance concrete systems¹.

Before life cycle cost analysis can be successfully applied to any system, an estimate of its service life must be available. For concrete, this requires knowledge of the chemical composition of the concrete materials, characterization of the intended exposure environment, estimates of the transport and mechanical properties of the concrete, and a hypothesis of the controlling degradation mechanism. While transport and mechanical properties can be measured (although sometimes with extreme difficulty), this direct approach provides little understanding of how to improve the materials. For this, it is necessary to establish linkages between processing, microstructure, and properties, the basic triad of all materials science. The microstructure of concrete (as with most materials) can be easily viewed in two dimensions, but it is the actual three-dimensional arrangement of phases that is critical in influencing performance properties. Three-dimensional x-ray microtomography is one promising technique for directly viewing the 3-D microstructure of building materials², but is limited in resolution to features on the order of several micrometers, just at the edge of the size range of importance for cement paste microstructure. A second promising approach to understanding the linkages between microstructure and properties is the use of computer modeling³. In this paper, the application of a set of multi-scale three-dimensional computer models^{4,5} to simulating the microstructure and diffusion properties of cement-based materials will be elucidated.

COMPUTER MODELING OF MICROSTRUCTURE

The NIST computer models consider the concrete microstructure at three different scales: 1) the nanometer scale where the key microstructural feature is the structure of the calcium silicate hydrate (*C-S-H*) gel, 2) the micrometer scale, which considers the multi-phase nature of the microstructure of hydrated cement paste, and 3) the millimeter scale, which takes into account the three-phase concrete microstructure consisting of aggregates (and air voids), their surrounding interfacial transition zones (ITZs), and bulk cement paste. Here, we shall provide a brief overview of the models employed at each scale, and discuss the special influence of silica fume at each microstructural scale. All of these models are documented and available (free of charge) for downloading over the Internet⁶.

Nanometer-Scale Microstructure

At the scale of nanometers, partially overlapping spherical particles are used to model the nanostructure of the *C-S-H* gel phase⁴. At this scale, we consider a two-phase composite, consisting of the *C-S-H* gel solid and the interconnected nanometer-scale pores (nanoporosity). This model is implemented in continuum space using a generalized hard core/soft shell (HCSS) 3-D microstructural model⁷. The porosity and size of the spherical particles have been set to values consistent with experimental data^{8,9}. Very recently, the nanostructure of a synthetic *C-S-H* gel has been directly observed using atomic force microscopy¹⁰, and appears to be quite

consistent with a structure based on a random agglomeration of spherical nodules, as were previously published transmission electron microscopy images¹¹.

It has been known for many years that the pozzolanic *C-S-H* gel that forms from the pozzolanic reaction between silica fume and calcium hydroxide (CH) has a different Ca/Si ratio and water content than the *C-S-H* gel formed from conventional hydration¹². Recently, Baroghel-Bouny¹³ has suggested that, additionally, the total porosity of pozzolanic *C-S-H* gel is about 19 %, in comparison to 28 % for conventional *C-S-H* gel. A lower porosity gel would also be expected to exhibit lower transport coefficients (perhaps partially accounting for the significant reductions in diffusivities and permeabilities generally observed with the use of silica fume). Using the HCSS model, the overall porosity is easily varied to examine its influence on the inherent diffusivity of the *C-S-H* gel, as will be presented below.

Micrometer-Scale Microstructure

At the scale of micrometers, the microstructure of cement paste exhibits complex spatial patterns. The initial cement particles vary in diameter (from about 1 μm to 100 μm) and many of the particles are multi-phase as well. Some hydration products form close to the initial cement particle surfaces, while others nucleate and grow within the water-filled capillary pore space. To attempt to capture this complexity, a cellular-automaton-based 3-D microstructural development model for cement hydration has been developed and refined^{14,15}. The starting point for the model is a collection of digitized spherical cement particles in water that matches the following characteristics of the cement being studied: 1) particle size distribution, 2) bulk mineralogical composition (phase volume fractions), 3) surface mineralogical composition (phase surface fractions), and 4) the two-point correlation structure of its mineral phases¹⁵. The two-point correlation functions quantify the spatial correlations amongst individual and groups of phases, answering questions of the form: If I am located in phase A, what is the probability that if I move a distance x away, I will still be in phase A? The matching of the "model" cement powder to its experimental counterpart greatly increases the likelihood of successfully predicting the real material's hydration behavior and property development. Typically, for this model, each pixel is 1 μm^3 in volume and system sizes are between 100³ pixels and 200³ pixels.

Hydration is modelled as a series of dissolution/diffusion/reaction cycles, during which the appropriate molar and volume stoichiometries for all of the cement hydration reactions are maintained¹⁴. Because the cement hydration products occupy less space than the reactants, under sealed curing conditions, empty capillary pore space must be created within the microstructure to account for this chemical shrinkage. These "hydration processes" may be conveniently simulated within the cellular automaton framework. The hydrated microstructure is available at any degree of hydration of interest for the subsequent computation of properties using finite element or finite difference techniques¹⁶.

At the scale of micrometers, silica fume participates in the cement hydration re-

actions, reacting both with CH and with conventional *C-S-H* gel, to form pozzolanic *C-S-H* gel^{12,17}. The activation energy for the pozzolanic reaction, on the order of 80 kJ/mol^{18,19}, is about double that for cement hydration, so that the pozzolanic reactions are much more sensitive to curing temperature. Because some additional water is incorporated into the pozzolanic *C-S-H* gel, the pozzolanic reaction further reduces the capillary porosity of the cement paste (and its transport coefficients as well).

Millimeter-Scale Microstructure

For the microstructure of concrete at the millimeter scale, we return to the HCSS model and simulate a three phase concrete consisting of spherical or ellipsoidal aggregates, their surrounding ITZ regions, and bulk cement paste. This basic model can be easily extended to examine a wide variety of issues specific to high-performance concretes (HPCs), such as the incorporation of ellipsoidal fibers to examine their effects on the percolation of ITZs and spalling susceptibility of HPC exposed to a fire²⁰, or the addition of saturated lightweight aggregates to provide internal curing for a low w/c ratio concrete²¹. For these simulations, a typical simulation volume is on the order of 27 cm³ of concrete, requiring up to one million individual aggregate particles (following any user-specified particle size distribution). The model code⁷ provides for microstructure generation, examination of the percolation properties of the ITZ regions, systematic point sampling to determine phase volume fractions, and execution of random walker algorithms for assessing the relative diffusivity of the 3-phase concrete composite (to be discussed in more detail below).

The major influence of silica fume at the concrete microstructure scale is to densify the ITZ regions^{22,23}. Whereas, after hydration, a typical ITZ region may be 20 μm thick in ordinary concrete, a value of 10 μm is more likely in a concrete with silica fume. The very small (< 1 μm in diameter) silica fume particles fill in the spaces between the larger cement particles. Because the silica fume particles are relatively evenly distributed within the capillary water and there is more capillary water in the ITZ regions (due to inefficient packing of the cement grains near the aggregate surfaces), there is actually a higher volume fraction of silica fume in the ITZs than in the bulk paste^{23,24}.

COMPUTATION OF DIFFUSIVITY

Electrical Analogy

At both the nanometer and micrometer scales, an electrical analogy is used to compute the relative diffusivity of the composite media²⁵, where relative diffusivity is the ratio of the diffusivity of an ion in the composite media relative to its value in bulk water (the inverse of the formation factor). For the *C-S-H* gel nanostructure model, the continuum volume must first be digitized into a cubic array of pixels, while for the cement paste microstructure model, the underlying pixel framework is easily mapped directly into a 3-D grid of resistors^{16,25}. Conductivities are assigned to each phase comprising the microstructure and the resultant composite relative

conductivity is computed¹⁶ and related to a relative diffusivity using the Nernst-Einstein relation²⁵:

$$\frac{D}{D_0} = \frac{\sigma}{\sigma_0} \quad (1)$$

where σ/σ_0 is the computed relative conductivity and D/D_0 is the relative diffusivity for the random microstructure.

Random Walkers (Blind Ants)

At the millimeter scale, the concrete microstructure cannot be easily digitized, due to the large size difference between the coarse aggregates (centimeters) and the ITZ thickness (some 20 μm). Thus, instead of using an electrical analogy, the relative diffusivity of the concrete composite is estimated using random walkers randomly distributed within the continuum microstructure^{7,26}. Each walker carries its own clock and keeps track of both the current time elapsed and the current distance from its starting location. With a large number of walkers (tens of thousands) taking a large number of random steps (hundreds of thousands), the relative diffusivity (or conductivity) of the concrete can be estimated⁷. For most concretes, the aggregates are assigned a diffusivity/conductivity of zero and thus, the walkers are prohibited from entering the aggregate particles. The ITZ regions are assigned a diffusivity either greater than, equal to, or less than that of the bulk paste²⁴, which is assigned a value of 1 for the random walker algorithm. The final result is then simply scaled by the real diffusivity of the bulk paste to obtain a "real" concrete diffusivity.

Linking the Micrometer and Millimeter Scales to Estimate Concrete Diffusivity

To compute the chloride ion diffusivity of a concrete containing a specific addition of silica fume^{5,24}, it is necessary to combine the models for the micrometer and millimeter scales in the following manner:

- 1) the "median" cement particle diameter is used to establish the thickness of the ITZ, t_{ITZ} , surrounding each aggregate,
- 2) the HCSS model is executed for the volume fraction and particle size distribution (PSD) of aggregate and t_{ITZ} of interest to determine the volume fractions of bulk (V_{bulk}) and ITZ (V_{ITZ}) cement paste (alternatively, the analytical equations of Lu and Torquato^{27,28} can be used for this determination),
- 3) these paste fractions are duplicated in the cement paste microstructural model in a system containing a single flat plate aggregate with the desired cement PSD, overall w/c ratio, and silica fume addition,
- 4) the cement paste microstructure is hydrated for a fixed number of cycles or until a degree of hydration of interest is reached,
- 5) the hydrated microstructure is analyzed to determine the capillary porosity present as a function of distance from the aggregate surface,

6) these local porosities and the initial local silica fume concentration (mass basis relative to cement) are substituted into a previously developed equation relating relative diffusivity of cement paste to capillary porosity and silica fume addition¹⁷ (eqn. 2),

7) the local relative diffusivities are averaged into two subsets- those within the ITZ region and those within the bulk cement paste,

8) the ratio of "average" ITZ diffusivity (D_{ITZ}) to average bulk cement paste diffusivity (D_{bulk}) is computed and used as input back into the HCSS model to determine the effective diffusivity of the concrete composite relative to that of the bulk cement paste using random walker techniques, and

9) finally, the overall diffusivity of the concrete is computed by multiplying the result of step 8 by the average bulk cement paste relative diffusivity determined in step 7 and by the diffusivity of chloride ions in bulk water (taken to be $1.81 \times 10^{-9} \text{ m}^2/\text{s}$ at 20°C for this study²⁹).

RESULTS AND DISCUSSION

Diffusion Coefficients at Each Scale

At the nanometer scale, the *C-S-H* gel nanostructures were digitized at a resolution of 1.25 nm/pixel into three-dimensional digital images with 200 pixels on a side. Based on the electrical analogy, the relative diffusivities computed for the pozzolanic *C-S-H* gel nanostructure are about a factor of five lower than those computed for the conventional *C-S-H* gel¹⁷. The formation factor (the diffusivity of the ion in bulk water divided by its diffusivity in the composite medium) computed for the conventional gel, 230, is slightly lower than the value of 400 that is typically used in the cement paste microstructure model to provide good agreement with experimental chloride ion and tritiated water diffusivity data^{17,25}.

Maintaining the ratio of five and using formation factors of 400 and 2000 for conventional and pozzolanic *C-S-H* gel, respectively, good agreement is obtained with the experimental data of Delagrave et al.³⁰ for tritiated water diffusion coefficients for cement pastes with w/c ratios of 0.25 and 0.45 and silica fume replacements of 0 % and 6 % on a mass basis¹⁷. However, to obtain agreement with the chloride ion diffusion data of Jensen²⁹, it was necessary to further increase the formation factor of the pozzolanic *C-S-H* gel to a value 25 times that of the conventional *C-S-H* gel¹⁷. With this value, excellent agreement was obtained between simulation and experimental data for w/c=0.3 cement pastes with 0 %, 3 %, 6 %, and 10 % silica fume additions. However, for the 20 % silica fume addition, the experimental diffusivity was still a factor of ten below the model-predicted value, suggesting the possibility of further modification of the nanostructure of the *C-S-H* gel at very high silica fume additions.

Using the values of 400 and 10,000 for the formation factors of the two types of *C-S-H* gel, a set of computer experiments was conducted to determine the effects

of w/c ratio, silica fume addition, and degree of hydration on relative chloride ion diffusivity of cement pastes¹⁷. The results are summarized in Fig. 1, which plots the computed relative diffusivity vs. total capillary porosity for the 67 systems examined (w/c between 0.2 and 0.7 and silica fume additions between 0 % and 20 %). The results can be conveniently fitted to a percolation-based equation of the form^{17,25}:

$$\frac{D}{D_0}(\phi, CSF) = \frac{0.0004}{\beta(CSF)} + \frac{0.03}{\beta(CSF)} \cdot \phi^2 + 1.7 \cdot (\phi - \phi_c)^2 H(\phi - \phi_c) \quad (2)$$

where D is the diffusivity of chloride ions in the cement paste, D_0 is their corresponding diffusivity in bulk water, ϕ is the capillary porosity, CSF is the silica fume addition (mass fraction of silica fume added per mass of cement), ϕ_c is the capillary porosity at which the capillary pore space depercolates (0.17), H is the Heaviside function ($H(x) = 1$ for $x > 0$ and 0 otherwise), and $\beta(CSF)$ is a function of the silica fume addition which can be approximated by the following equation composed of three individual parts for low, intermediate, and high CSF additions, respectively²⁴:

$$\begin{aligned} \beta(CSF) &= 1.0 & CSF &\leq 0.025 \\ \beta(CSF) &= 1.0 - 48.6CSF + 2330 \cdot (CSF)^2 - 11400 \cdot (CSF)^3 & 0.025 < CSF &\leq 0.12 \\ \beta(CSF) &= 9.0 & CSF &> 0.12 \end{aligned} \quad (3)$$

As can be seen in Fig. 1, the fits of eqn. 2 to the simulated data are quite reasonable. While the capillary porosity remains percolated ($\phi > 0.2$), the data collapse onto a single curve as the highly conductive path through the connected capillary pores controls the diffusivity. But, once the capillary porosity depercolates, the curves diverge into separate lines for each silica fume content, as now, the diffusivity is controlled by transport through the two types of $C-S-H$ gel and their percolation characteristics¹⁷.

At the concrete scale, silica fume affects diffusivity by densifying the ITZs surrounding each aggregate particle. This effect can be seen in Fig. 2, which contrasts the variation in capillary porosity with distance from the surface of an aggregate particle for w/c=0.4 cement pastes with silica fume additions of 0 % and 10 %. Because we are considering a silica fume addition, the initial overall porosity is slightly reduced in the 10 % system due to the additional volume occupied by the silica fume. Still, after hydration, the overall porosity is further reduced, due to the pozzolanic reaction, and the porosity gradient in the ITZ region is significantly reduced. This improvement in microstructure is achieved despite the fact that after the 2000 cycles of hydration, the degree of hydration of the cement in the 0 % silica fume system is 0.843, while that in the one with 10 % silica fume is only 0.775 (due to water availability/space limitations).

Recently, a full factorial computer experiment has been conducted to develop an equation to predict the chloride ion diffusivity of a concrete as a function of w/c ratio,

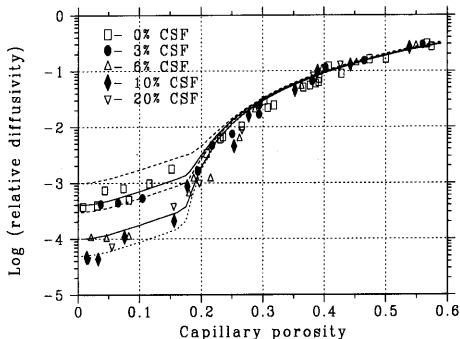


Figure 1: Model results for relative diffusivity of cement pastes with silica fume vs. total capillary porosity¹⁷ at 20 °C. Top dashed line indicates a previously developed equation²⁵. Lower four lines (solid and dashed) from top to bottom indicate fits for 0 %, 3 %, 6 %, and 10 % silica fume additions, respectively.

silica fume addition, volume fraction of aggregates (V_{agg}), and degree of hydration of the cement (α)²⁴. A total of 36 different concrete mixtures were examined using the computational techniques outlined above, resulting in the following predictive equation for concrete diffusivity as a function of mixture proportions and expected degree of hydration²⁴ at 20 °C:

$$\log_{10}(D) = -13.75 - 0.82\left(\frac{w}{c}\right) + 32.55\left(\frac{w}{c}\right)^2 + 8.374(CSF) + 15.36(CSF)^2 + 23.15\left(\frac{w}{c}\right)(CSF) + 5.79\alpha - 21.10\left(\frac{w}{c}\right)(\alpha) - 43.15(CSF)(\alpha) - 1.705 V_{agg} \quad (4)$$

where D is in units of m^2/s . Equation 4 accurately predicts the model-computed chloride ion diffusion coefficients over a range encompassing nearly three orders of magnitude²⁴ and can be used to estimate the diffusivity of any concrete of known

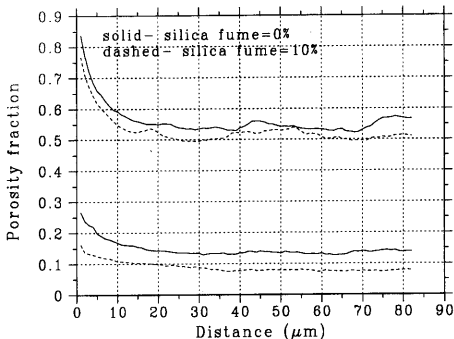


Figure 2: Model results for capillary porosity fraction vs. distance from center of aggregate surface for $w/c=0.4$ concretes hydrated for 2000 cycles using the NIST model²⁴. Top two lines indicate initial capillary porosities and lower two correspond to capillary porosities after hydration.

composition and maturity within the range of concretes investigated (w/c between 0.3 and 0.5, silica fume additions between 0 % and 10 %, V_{agg} between 0.62 and 0.70, and α between 0.6 and 0.9).

Equation 4 can also be used to predict the relative improvement in diffusion resistance offered by various levels of added silica fume. This is most easily formulated as the multiplicative increase in diffusion resistance for a given silica fume addition (due to the logarithm form of eqn. 4) and specific values of w/c ratio and degree of hydration. In this case, the multiplicative increase is given by:

$$\frac{D(CSF = 0)}{D(CSF)} = 10^{-[(8.374 - 43.15\alpha + 23.15\frac{\alpha}{c}) - CSF + 15.36(CSF)^2]} \quad (5)$$

Since both w/c and α are variables in eqn. 5, one can fix α and plot the variation in the dependent variable with w/c ratio for four different silica fume additions (2.5 %, 5 %, 7.5 %, and 10 %).

5 %, 7.5 %, and 10 %). Figure 3 provides an example of the results for $\alpha = 0.675$. In this figure, it is clear that silica fume is more effective in reducing diffusivity in lower w/c ratio concretes. For the lower w/c ratios (e.g., 0.3), the addition of 10 % silica fume may decrease the chloride ion diffusivity by a factor of 15 or more.

A more quantitative evaluation against experimental data can be made using the data set of Hooton et al.³¹, who measured concrete diffusivity by a number of methods for three different water to cementitious material (w/s) ratios and three different silica fume replacement levels. For comparison purposes, we shall consider their diffusion results generated in the long term, from a modified chloride ponding test³¹, although it is worth noting that the relative improvement provided by the silica fume is nearly constant for all of the different measured "diffusion" coefficients³¹. This, in spite of the fact that for a given concrete, the different tests may produce results that vary by up to a factor of three. Because, in the current computer experiment, w/c ratio is maintained constant and silica fume additions are considered, the experimental data must first be transformed to the same parameter space. Thus, the w/s=0.35 mixture with 12 % silica fume replacement corresponds very closely to a w/c=0.4 mixture with 13.8 % silica fume addition. Similarly, the w/s=0.4 mixture with 7 % silica fume replacement corresponds to approximately a w/c=0.44 mixture with 7.7 % silica fume addition. Assuming that the degree of hydration of all of the concretes is 0.675, the experimental results are plotted along with the simulation data in Fig. 3. The agreement between experimental data and simulation results appears reasonable for these two data points.

Complications at Each Scale

While the above simulation results appear promising, both in offering insights into the relations between microstructure and diffusion coefficients and in predicting experimental performance, they are of course based on a simplified (but still rather complex) view of reality. Thus, it seems appropriate to comment on the complications existing at each scale considered by the microstructure models.

At the nanometer scale, the nanostructure of the *C-S-H* gel is a dynamic system that changes with time (polymerization), moisture content (shrinkage), and load (creep). The quantitative effects of these parameters on nanostructure and transport properties are largely unknown. As the *C-S-H* gel polymerizes under stress and time, it likely expels some gel water^{32,33}, producing a denser, less diffusive gel, and possibly providing capillary water for renewed cement hydration³².

At the micrometer scale, cement paste in a field concrete is rarely saturated. Since chloride ions will only diffuse in the capillary pores which are water-filled, this will generally result in a reduction in measured diffusivity. For the case of self-desiccation, simulations³⁴ have indicated that the computed diffusion coefficients still basically follow the top solid line shown in Fig. 1 when the x-axis is changed to water-filled capillary porosity as opposed to total capillary porosity. An excellent summary of the many phenomena requiring consideration for the proper modeling of diffusion in partially saturated concrete has been provided by Saetta et al.³⁵

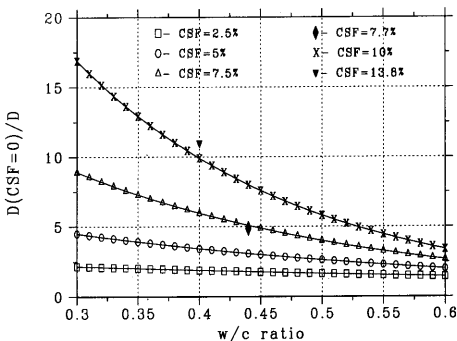


Figure 3: Computed multiplicative increase in diffusion resistance due to silica fume addition vs. w/c ratio for an assumed degree of hydration of 0.675²⁴. Filled data points indicate the experimental data of Hooton et al.³¹

Some additional theoretical considerations and worked-out model computations have been reported by Martys³⁶. Another consideration at the micrometer scale is the microcracking of the cement paste. If the microcracks are relatively fine and not percolated, their effects on diffusive transport should be minimal, however³⁷.

A possibly more important concern regarding diffusive transport at the scale of micrometers is the leaching of calcium hydroxide and other phases from the cement paste. Simulations³⁸ have indicated that the complete removal of calcium hydroxide from a well hydrated cement paste can increase its relative diffusivity by up to a factor of 40, due to repercolation of the disconnected capillary porosity network. Experimental measurements of the effects of leaching on the diffusion coefficients of chloride ions²⁹ and cesium and tritium³⁹ have been performed, and in the latter case, there is good agreement between the experimental data and model predictions⁴⁰. Similarly, the precipitation of ettringite and Friedel's salt within the capillary pore

network could result in reductions in the measured diffusion coefficients.

At the concrete scale, the spatial heterogeneity of the microstructure must be properly considered. Most cast concrete surfaces will have an increase in paste fraction (and a concurrent decrease in aggregate content) as the cast surface edge is approached^{5,41}. Thus, the top 5 mm to 10 mm of the concrete may have a different diffusion coefficient than the bulk concrete (due both to this spatial "wall" effect and to in-place curing or lack thereof). This spatial heterogeneity in diffusivity can be modelled by considering a two-layer concrete, where the diffusion coefficient of the surface layer is higher (or lower) than that of the bulk layer. Both analytical solutions⁴² and direct finite difference calculations⁴³ can be developed to simulate this scenario.

CONCLUSIONS

A set of multi-scale three-dimensional microstructural models have been applied to develop equations to predict the influence of mixture proportions (including silica fume addition) and maturity on the chloride ion diffusivity of concrete. The models appear to offer the flexibility to consider further complexities (*C-S-H* creep, drying/resaturation, etc.) as more quantitative experimental data on these phenomena becomes available. Based on the computer modeling, the volume fractions and percolation characteristics of the phases responsible for transport (capillary porosity and the two kinds of *C-S-H* gel) regulate the diffusivity of cement-based materials. The addition of silica fume decreases transport coefficients both by reducing capillary porosity and by producing a *C-S-H* gel with decreased transport coefficients in comparison to that produced during conventional cement hydration. The effects of silica fume are especially prominent at low *w/c* ratios. For example, for *w/c*=0.3, a 10 % addition of silica fume may reduce the chloride ion diffusivity of a concrete by a factor of fifteen or more.

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