Concrete: A Multi-Scale Interactive Composite

by

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CONCRETE: A MULTI-SCALE INTERACTIVE COMPOSITE

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Abstract

Methods have been developed for predicting the overall diffusion coefficient of ions in concrete using a multi-scale interactive analysis, ignoring any chloride binding interactions. The analysis makes use of microstructure models of mortar/concrete and cement paste at the scales of millimeters and micrometers, respectively. When comparing experimental data to model results, one must be careful to consider the differing w/c ratio and degree of hydration in the interfacial transition zone (ITZ) and bulk paste regions, relative to a cement paste specimen containing no aggregates. The amount of aggregates influences the amount and properties of these two cement paste phases, leading to the designation of concrete as an *interactive composite*. The multi-scale analysis presented in this paper can quantitatively take this interaction of aggregates and cement paste into account. when modelling the properties of concrete in terms of its microstructure. The analysis predicts that the contrast in diffusivity between the ITZ and the bulk cement paste is a function of the degree of hydration.

Keywords: Concrete, diffusivity, interfacial transition zone, microstructure, modelling, multi-scale

1 Introduction

One example of the complexity of the microstructure of concrete is found in the nature of the interfacial transition zones (ITZ) existing between aggregate and cement paste [1]. Due to an inefficient packing of cement particles near the aggregate, the ITZ regions are generally more porous and contain less unhydrated cement than the surrounding paste [2, 3]. This gradient of microstructure modifies the mechanical and transport properties of the concrete, so that the concrete must be considered as (at least) a three-phase material and not simply as a composite of aggregates in a matrix [4, 5, 6, 7].

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The large range of length scales necessary for modelling concrete require a multi-scale approach, where separate models have been developed for the millimeter (mortar/concrete) and micrometer (cement paste) scales [8]. By integrating these models, **a** complete calculation of the chloride diffusivity of a concrete may be obtained [9, 10]. This paper reviews this multi-scale analysis and presents evidence. validated by experimental data, that the contrast in properties between ITZ and bulk cement paste is a function of the degree of hydration and goes through a maximum as the cement hydrates. Needed refinements in the multi-scale analysis, as shown by experimental evidence, are **also** discussed.

2 Microstructural Modelling and Computational Techniques

2.1 Concrete Microstructure Model

For modelling concrete, a computational volume or box, of side dimension anywhere between **10** and **50** mm, is filled with spherical aggregates, each surrounded by a constant thickness ITZ [10, 11, 12], **as** shown in the left side of Figure **1.** This model is a continuum model, with each aggregate completely characterized by the coordinates of its center and the value of its radius. Once a microstructure has been created, the volume fractions of ITZ and bulk paste (paste outside of the ITZ regions) and the degree of connectivity of the ITZ regions are determined [9, **10,** 11] numerically or analytically. The connectivity of these ITZ regions across a **3-D** concrete microstructure has recently been verified experimentally [13].

2.2 Cement Paste Microstructure Model

A cement hydration model is used to simulate and analyze the microstructure and properties of a single ITZ [14]. The cement powder to be modelled is represented by non-overlapping digitized spheres following the particle size distribution (PSD) measured on actual cement samples, with each pixel element representing **1** μm^3 in volume. A single flat plate aggregate is placed in the center of the microstructure before placing any of the cement particles (see lower part of the right side of Figure 1). The dimensions of the computational **box** are adjusted so that the appropriate volume ratio of ITZ to bulk cement paste is obtained, matching that previously determined using the concrete microstructure model.

After initial particle placement, microstructure development due to the hydration reactions between cement (tricalciurn silicate) and water are modelled [14]. At any degree of hydration, the porosity present **as** a function of distance from the aggregate surface can be determined. 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. During hydration, the porosity is reduced throughout, but it still remains higher in the ITZ regions. Thus, these regions will have a higher diffusivity than the bulk paste regions. The relative diffusivity (D/D_0) as a function of distance from the aggregate surface, x, can be

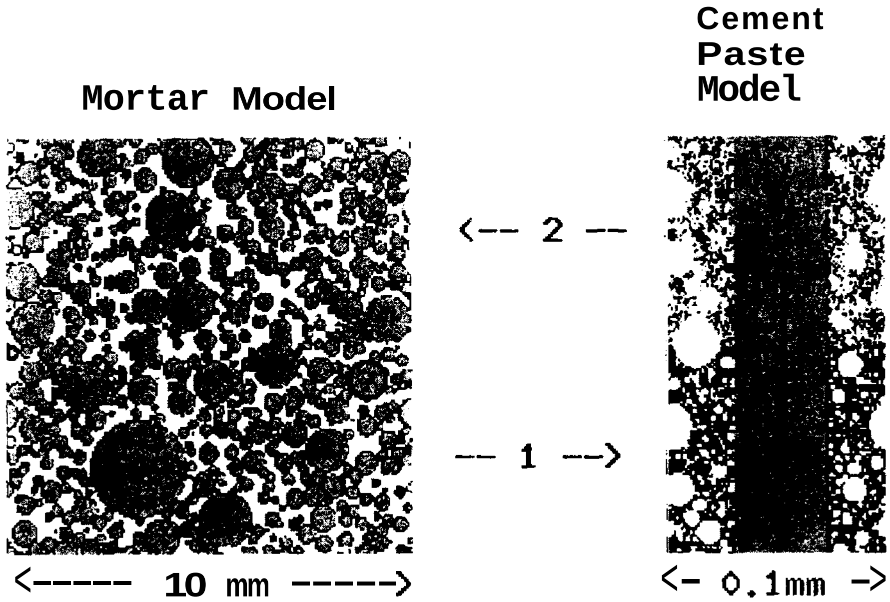

Figure 1: Linkages between microstructure models for mortar/concrete and cement paste in the multi-scale analysis. In the mortar model, inclusions are grey, ITZ regions are black, and bulk paste is white. In the cement paste model, cement particles are white, water-filled porosity is black, and the flat rectangular aggregate is grey. In the hydrated image (upper right), calcium hydroxide is dark grey and calcium silicate hydrate gel is light grey. The arrows indicate the flow of information between the models, and are explained in the text. The dimensions given are typical for each kind of model.

estimated using the equation [15]:

$$\frac{D}{D_0}(x) = 0.001 + 0.07.\ \phi(x)^2 + 1.8.\ H(\phi(x) - 0.18).(\phi(x) - 0.18)^2 \qquad (1)$$

where relative diffusivity is defined as the ratio of the diffusivity of ions in the material of interest relative to their value in bulk water, $\phi(x)$ is the porosity fraction at a distance x, and H is the Heaviside function having a value of 1 when $\phi > 0.18$ and a value of 0 otherwise.

2.3 Multi-Scale Simulation Procedure

The multi-scale analysis is illustrated for a mortar in Figure 1 (the arrows in Fig. 1 show the Aow of information between the two microstructure models and their parts). Initially, the median particle diameter of the cement PSD is used to establish the ITZ thickness, t_{ITZ} [12]. Aggregate particles following the aggregate

PSD are placed into the mortar volume. The volume fractions of interfacial transition zone (V_{ITZ}) and bulk (V_{bulk}) paste for this choice of aggregate PSD and t_{ITZ} (9, 10, 11] are then determined. The computational box dimensions for the cement paste model are chosen to match this ratio of V_{ITZ}/V_{bulk} (arrow 1 in Fig. 1). Cement particles are placed into this computational volume to achieve the desired w/c ratio. and the hydration model is executed to achieve the chosen degree of hydration (vertical arrow). It is by this step that the redistribution **of** cement between ITZ and bulk cement paste is approximately computed. The porosity of the cement paste is then measured as a function of distance from the aggregate surface and converted to relative diffusivity values using Eqn. 1. These values are averaged in two subsets, those lying within t_{ITZ} of the aggregate and those in the bulk paste, in order to give the values of D_{ITZ}/D_0 and D_{bulk}/D_0. The ratio of these two diffusivities, D_{ITZ}/D_{bulk}, is then used as an input back into the original concrete model (arrow **2** in **Fig.** 1). Of course. using a different value of t_{ITZ} would give a different value of D_{ITZ}/D_{bulk} [16]. Using the median particle diameter of the cement is probably the most realistic measure to use, however. The diffusivity of the overall concrete system, D_{conc}/D_{bulk}, is then computed [9, 10] At this point, the concrete consists of aggregates with a diffusivity of 0, bulk paste with a diffusivity of 1, and interfacial transition zones with a diffusivity of D_{ITZ}/D_{bulk}. This value can then be converted into an absolute chloride ion diffusivity for the concrete, D_{conc}, by multiplying it by D_{bulk}/D_0 as determined from the cement paste microstructure model and by D_0, the diffusion coefficient of chloride ions in bulk water [9, 17].

3 Results

3.1 Overall concrete diffusivity

Because of the local rearrangement of the cement. particles in the vicinity of each aggregate, the ITZ w/c ratio will be significantly higher than that of the bulk cement paste in a concrete. Since the overall w/c ratio of a concrete mixture is determined at mix time, the bulk w/c ratio will therefore be less than this nominal value. To illustrate this effect, Figure **2** provides a plot of the initial distribution of anhydrous cement and water in a typical concrete with an ITZ thickness of 20 μm. The w/c ratio in portions of the ITZ region is seen to be over twice that of the nominal value of **0.45** and the bulk paste is seen to have a w/c ratio on the order of 0.4, quite similar to experimental results by Scrivener and Pratt in Ref. [1]. As the surface area of the aggregates increases, there will be more ITZ paste in a concrete, and a greater decrease in the bulk w/c ratio relative to the nominal value. Because the surface area to volume ratio of an aggregate increases with decreasing size, this means that there should be a larger ITZ effect on properties in mortars than in concrete.

The overall diffusion coefficient of a concrete is determined by the competition between the value of D_{ITZ}/D_{bulk}, the value of D_{bulk}, and the zero diffusivity of the aggregates. In most concretes, the zero diffusivity of the aggregates and the

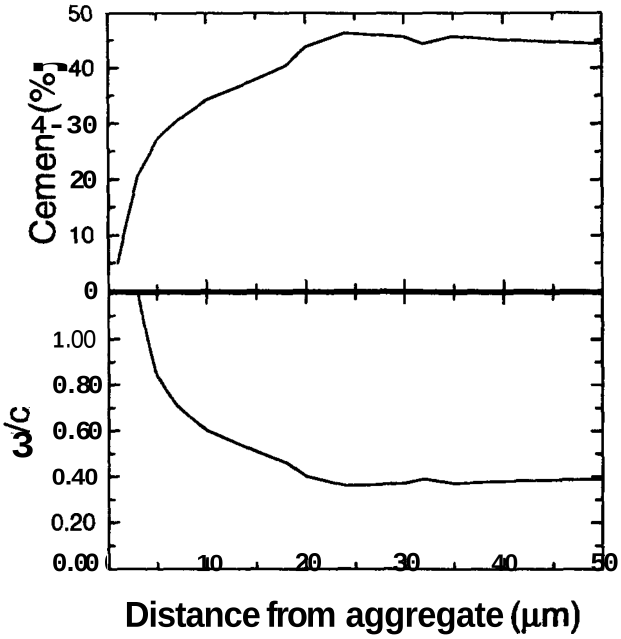

Figure 2: Initial distribution of anhydrous cement and w/c ratio in the ITZ for a concrete (overall w/c=0.45, 67.5% aggregate volume fraction.

value of D_{bulk} wins, so that the diffusivity of concrete is decreased by adding more aggregate, and has a lower diffusion coefficient than a cement paste of the same nominal w/c ratio. If the diffusivity of the ITZ regions were high enough, adding more aggregates *to* the concrete could actually increase the chloride ion diffusion coefficient above that of the equivalent cement paste [5]. This may be the case in some fine-sand mortars [18]. When considering fluid permeability, the usual case is for the concrete to have a much higher permeability than cement paste with the same nominal w/c ratio [19]. It is likely that the ITZ to bulk cement paste contrast is much higher in this case, so that adding aggregates would probably increase the permeability of the concrete.

3.2 D_{ITZ}/D_{bulk} vs. degree of hydration

The multi-scale model computes the value of D_{ITZ}/D_{bulk} for different degrees of hydration α. This parameter has sometimes been discussed as if it were a single number and not a function of α. However, eq. (1), which gives the diffusivity of cement paste as a function of porosity, is a non-linear function. Also, the porosities in the ITZ and bulk regions are simple, but different, linear functions of α. Therefore, the ratio D_{ITZ}/D_{bulk} is also a function of α.

Figure 3 shows model results for this ratio as a function of α for two different

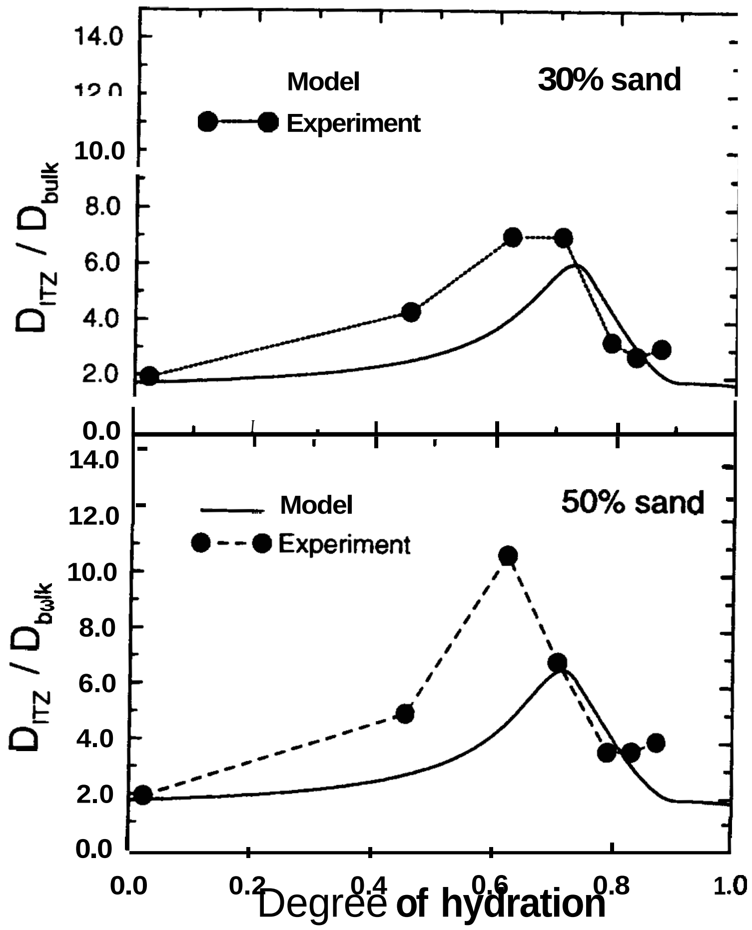

Figure 3: The computed value of D_{ITZ}/D_{bulk} as function of the degree of hydration for two mortars with the same cement and the same aggregate PSD, but with 30% and 50% sand volume fraction.

mortars, one with **30%** and one with 50% sand by volume. The peak in the model results comes at about $\alpha = \mathbf{0.70}$. The experimental data points are from recent work on the electrical conductivity of mortars **as** a function of sand content and ITZ properties [20] (recall that electrical conductivity and ionic diffusivity are mathematically equivalent in this case). Reasonably good agreement is seen for the **30%** sand mortar, with a greater difference between model and experiment. for the 50% sand content mortar. In particular, the height of the experimental curve is not reached by the model prediction for the 50% sand mortar. Also, the experimental curves tend to peak slightly earlier in α for both mortars. At late hydration, the agreement between model and experiment is much improved. For durability studies, the predictions of the model will then be more reliable, since for service lives in years, higher degrees of hydration undoubtedly have occurred. Further detailed comparison between experiment and model data is found in Ref. [20].

4 Discussion and Summary

The agreement between model and experiment seen in Fig. **3,** especially after substantial hydration, is encouraging. The discrepancies show that the model needs some refinement, however. In particular, eq. (1) probably needs to be looked at again, in light of improvements to the cement paste microstructure model made since it was developed [14]. Also, the way the parameter D_{ITZ}/D_{bulk} was extracted from experiment was by using a differential effective medium theory [10, 20]. This effective medium theory can also most likely be improved, which would affect the values of this parameter extracted from experiment . Finally, the distribution of hydration products between ITZ and bulk cement paste is probably not handled quite correctly at intermediate degrees of hydration by the cement paste microstructure model, judging by the disagreement shown in Fig. **3.** The model is flexible in this area, and can probably be calibrated to predict this distribution more accurately.

Multi-scale microstructure models have been applied to simulating the development of ITZ microstructure in concrete and computing its effects on diffusivity. The model provides quantitative insights into the increased w/c ratio and porosity of the ITZ regions and the concurrent reduction in bulk paste w/c ratio and porosity. Details of the model can be systematically improved, which may improve the agreement with experiment.

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