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Multi-Aggregate Approach for Modeling Interfacial Transition Zone in Concrete

by Hongyan Ma and Zongjin Li

Interfacial transition zone (ITZ) has long been of particular interest in concrete technology. The limited sensitivity of experimental techniques makes it attractive to study ITZ using computer simulations. In this paper, a multi-aggregate approach is proposed to simulate the formation of ITZ in concrete. In light of a modified status-oriented computer model for simulating cement hydration, the evolution of ITZ is also simulated in this approach. Through simulations, the influences of several factors related to concrete mixture proportion on ITZ are investigated. It is found that ITZ thickness, as defined by the overall average porosity, can be reduced by using finer aggregate, increasing aggregate volume fraction, reducing water-cement ratio (w/c), or making the binder system finer. Following hydration, the ITZ thickness decreases continuously, but the difference of porosity between ITZ and bulk paste keeps almost constant at mature ages.

Keywords: interfacial transition zone (ITZ); ITZ thickness; multi-aggregate approach; porosity; simulation; status-oriented computer model.

INTRODUCTION

In concrete technology, it is a common view that mortar or concrete can be considered a composite consisting of aggregate, bulk paste, and ITZ, which is the weakest link considering both strength and permeability.¹⁻³ Thus, ITZ has long been of particular interest in studies on both mechanical and transport properties of concrete. Studies on ITZ began in the early 1950s, and some basic theories were published during that period.⁴ In the 1970s, using glass as “aggregate,” extensive studies on the structure of ITZ were carried out.⁵⁻⁷ Following these early findings, some researchers began to debate the reality of ITZ in real concrete.^{8,9} However, since the preliminary scanning electron microscopy (SEM) study of the microstructure of ITZ in mortar,¹⁰ the existence of ITZ in concrete and mortar has been proven by many techniques, including mechanical tests,¹¹ mercury intrusion porosimetry (MIP) tests,¹² and transport tests.¹ Neville¹³ has pointed out that ITZ exists around not only coarse aggregate particles but also fine aggregate particles down to the smallest particle size. The formation, evolution, and properties of ITZ have been extensively investigated. As demonstrated in these publications, the characteristics of ITZ include higher porosity, coarser pore structure, higher concentration and larger crystals of calcium hydroxide and ettringite than bulk paste, as well as less anhydrous cement grains.^{8,9,11,14-17}

In the last two decades, several computer models have been developed to study properties of ITZ.¹⁷⁻²⁵ These models are very effective in the characterization of ITZ, especially in obtaining the three-dimensional (3-D) gradi-

ents of parameters like porosity, degree of hydration, and calcium hydroxide content following the distance to aggregate surface. However, wall effect was considered as the unique mechanism of ITZ formation in these models, thus simple-shaped (cube, cuboid, or cylinder) simulation space was always selected, while rigid boundaries were used to simulate the aggregate surface and periodic boundaries the continuous cement paste. In this kind of model, other mechanisms contributing to the formation and evolution of ITZ—such as those introduced in this study—cannot be simulated, and the influences of technical parameters like aggregate particle size and aggregate volume fraction cannot be effectively considered.

In this study, a multi-aggregate approach is proposed to simulate the formation and evolution of ITZ in concrete, considering the influences from water-cement ratio (w/c), aggregate particle size, characteristic paste thickness (aggregate fineness and volume fraction), binder fineness, and degree of hydration. In the simulated properties of ITZ, thickness and porosity are given more attention because they are closely related to the percolation of ITZ and transport properties of concrete.

RESEARCH SIGNIFICANCE

This paper presents the simulations of the formation and evolution of ITZ in concrete, based on a newly developed multi-aggregate approach. Although considerable research has been conducted experimentally and numerically, the characteristics of ITZ, as represented by ITZ thickness or porosity distribution, have not been fully determined quantitatively. The multi-aggregate approach considers different mechanisms of ITZ formation and evolution, not limited to the wall effect. It has the potential to quantitatively predict ITZ characteristics, taking into account the influences of practical parameters such as w/c , characteristic paste thickness (aggregate fineness and volume fraction), and the degree of hydration (or age).

FORMATION AND EVOLUTION MECHANISMS OF ITZ

The wall effect is used broadly to explain the formation of ITZ.^{13,26-28} However, the wall effect is just one of the origins

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of ITZ and not effective enough to explain the evolution of ITZ. In the literature, different theories have been developed to understand the formation and evolution of ITZ.

Formation mechanisms of ITZ

Wall effect—During mixing and casting, the spatial arrangement of anhydrous cement particles becomes looser in the vicinity of aggregate particles. Consequently, in fresh concrete the porosity and w/c increase from the bulk to the surface of the aggregate.⁸ The difference in packing density leads to a gradient in particle density or porosity to an extent of 10 to 20 μm , or the mean particle size of cement.¹¹

Filtration effect—This effect, also called the two-wall effect,²⁹ occurs when two or more aggregates are lying close to each other and the cement particles get filtrated. As a result, only few small cement particles are left between these aggregate particles. In such regions, no bulk paste exists, and it can be considered as the overlapping of two or more ITZs.

Water film—Immediately after mixing, all the solid particles are covered at once by a water film. The thickness of the water film is a constant of approximately 10 μm around all particles.³⁰ The film around aggregate particles will lead to the porous ITZ. This is the simplest and perhaps earliest in the theories about the formation of ITZ.

Microbleeding—Some researchers^{1,3,30} reported that the relative movement of sand and cement grains during mixing may lead to regions of low paste density at the paste-aggregate interface. Bleeding water accumulates below larger aggregate particles, creating additional links of weakness.³⁰ This phenomenon is called localized bleeding or microbleeding. However, this kind of weakness is also present at the upper side of large aggregates, and microbleeding can occur and give more water to the area around aggregate particles due to other reasons, such as vibration and instability of cement paste.²⁹

Syneresis—Syneresis was introduced by de Rooij³¹ to study the formation of ITZ. During syneresis, the cement gel shrinks and the water comes out of the cement gel structure. This leads to a separation of a water-rich mass from a solid-rich mass. Similarly, a DLVO theory (colloid science) has been introduced to explain the formation of ITZ.^{32,33} Both of the theories are controlled by some colloid science parameters (such as zeta potential and ionic concentration), and have the potential to explain the varying properties of ITZ in different w/c cases and when it contains different admixtures.

In these theories, microbleeding and syneresis may be considered as the origins of water film. The three water film-related theories are different from the former two—which are related to particle packing—and are difficult to simulate in a static model without considering the physico-chemical processes. Thus, in the present study, only particle packing-related theories are considered as the formation mechanisms of ITZ.

Evolution mechanisms of ITZ

Nucleation and precipitation—This is the filling of water-rich regions in ITZ by hydration products, especially calcium hydroxide and ettringite, from outside of ITZ. In the early hydration process, the concentration of silicate is still very

low while that of calcium ions has been much higher in the pore solution. Consequently, the calcium silicate hydrates (CSH) mostly deposit around cement grains, while calcium hydroxide precipitates in open pores. Furthermore, silica inhibits the nucleation of calcium hydroxide, which favors the precipitation of calcium hydroxide as far from cement grains as possible. Thus, a lot of calcium ions migrate into the large water-filled spaces in ITZ and form large crystals with less nucleation sites.^{8,11} Nucleation onto solid surfaces from a mildly supersaturated solution is a common phenomenon; thus, calcium hydroxide may tend to deposit against aggregate surfaces.⁹

One-sided growth—Because CSH is mostly deposited around cement particles, only a small amount can be formed near the aggregate surface. In a small zone near an aggregate surface, solid volume growth induced by CSH formation occurs only from one side, as no CSH can be formed from the aggregate surface side. However, a space in bulk paste can be filled by CSH volume growth from more than one side.^{18,29}

The mineralogy and texture of the aggregate and the potential cracks in ITZ induced by shrinkage and thermal change in the service life of concrete may also be responsible for the microstructure evolution of ITZ.²⁹ However, it is difficult to consider these factors quantitatively in a cement hydration based computer simulation. Therefore, in this study, only nucleation and precipitation of crystal hydrates and the one-sided growth of CSH are considered as the main mechanisms governing the evolution of ITZ.

SIMULATION METHOD: MULTI-AGGREGATE APPROACH

In real concrete, the aggregate volume fraction is typically higher than 60%. With such high aggregate volume fraction, few ITZs exist independently, as most overlap with others. Hence, ITZ should be investigated as a statistical concept rather than one which can be obtained through one simple simulation. Simulations by packing cement particles in a simple simulation space with rigid boundaries cannot reflect the influences of parameters like aggregate particle size and aggregate volume fraction. For the sake of simulating the ITZ in concrete more realistically, a multi-aggregate approach is developed in this study.

Formation of ITZ

In the multi-aggregate approach, no simple-shaped simulation space is defined for the packing of cement particles. Spherical particles representing cement grains are randomly packed in a space restricted by an outer spherical surface and a series of smaller inner spherical particles representing aggregate particles. The space defined for packing cement grains is shown in Fig. 1. As compared with the small aggregate particles (inner ones), the outer surface is concave and its curvature is sufficiently smaller so that it can be used to simulate the surface of much larger aggregate particles. The term “multi-aggregate” means aggregate particles, as defined by the outer surface and the inner spherical particles, with the same physico-chemical properties except particle

Fig. 1—Space for packing cement grains as defined in multi-aggregate approach, in which both outer surface and inner particles are used to simulate aggregate particles.

size. The outer surface and all surfaces of small aggregate particles are treated as rigid boundaries for cement particles.

Given the mixture proportion of a concrete or a mortar, the aggregate volume fraction (V_{agg}) can be easily calculated, then the volume fraction of paste (the summation of bulk paste and ITZ) $V_p = 1 - V_{agg}$. With the aggregate PSD (particle size distribution) function, and assuming that all aggregate particles are spherical, one can also compute the surface area of aggregate per unit volume of concrete (S_{agg} , $length^{-1}$). A characteristic paste thickness t_p is defined herein as

$$t_p = \frac{2(1 - V_{agg})}{S_{agg}} \quad (1)$$

Herein, the t_p is just used as a parameter to ensure the comparability of the simulated concrete and the real concrete. Detailed theoretical studies about the average spacing between neighboring aggregates can be found in the literature.^{34,35} In simulations, after placing a series of small aggregate particles with the diameter of d_i into the pre-defined outer surface with the diameter of d_{os} , the simulated characteristic paste thickness t_p' can be calculated as

$$t_p' = \frac{d_{os}^3 - \sum d_i^3}{3(d_{os}^2 + \sum d_i^2)} \quad (2)$$

Only when t_p' equals to t_p can the system be used to simulate the ITZ in the target concrete. In the present study, d_{os} is fixed on 600 μm for balancing its representability and computing time. One 300 μm particle is selected as an inner particle, and the numbers of 200 μm and 100 μm particles are varied to meet the required t_p' . All the inner aggregate

Fig. 2—Central cross-sectional view of simulation system before hydration. (Note: $w/c = 0.5$, $t_p = 80 \mu m$.)

particles are randomly placed in the space defined by the outer surface, as shown in Fig. 1. After that, cement particles are sequentially packed into the space restricted by the outer surface and the inner particles according to w/c and the PSD function of cement. Cement PSD is assumed to be governed by the Rosin-Rammler function expressed as³⁶

$$P_v(d) = 1 - e^{-bd_n} \quad (3)$$

where $P_v(d)$ means the cumulative distribution function of cement particles in terms of volume; d is cement particle size; b is a constant related to the mean cement particle size; and n is a constant measuring the dispersion of particle diameters. In this paper, b is set as 0.034, and n is set as 1.09, corresponding to cement with a Blaine value of 360 m^2/kg and a mean particle diameter of 15.8 μm . Particles smaller than 1 μm are cut off to simplify the simulation. With cement PSD and the algorithm described by Zheng et al.,²⁴ one can generate the numbers of cement particles with various sizes based on paste volume and w/c . With the numbers, a sequential random generator-based algorithm is used to place cement particles into the space, from the largest to the smallest. The location of each cement particle is governed by randomly generated coordinates. Overlapped with the outer surface, inner aggregate particles and earlier generated cement particles will result in a rejection, whereupon the process continues. The process will not stop until all cement particles are located.

After placing all cement particles, the whole system is digitized into voxels with the size of $1 \times 1 \times 1 \mu m^3$, as shown in Fig. 2. In the figure, white, gray, and black represent unhydrated cement particles, aggregate particles, and pores (or water). Then, on a spherical surface with a distance d_s to the outer surface in its inward-pointing normal direction, or a spherical surface with a distance d_s to an inner aggregate

particle surface in its outer-pointing normal direction, the numbers of the three kinds of voxels can be counted and recorded, that is, the number of unhydrated cement voxels N_{uc} , the number of aggregate voxels N_{agg} , and the number of pore voxels N_{pore} . The porosity ϕ_{pore} on such a surface can be defined as

$$\phi_{pore} = \frac{N_{pore}}{N_{pore} + N_{uc}} \quad (4)$$

whereupon one can plot the local porosity ϕ_{pore} against the distance to the aggregate surface d_s and define the extent of ITZ on such a curve.

Evolution of ITZ

As aforementioned, the evolution of ITZ is assumed to be governed by the nucleation and precipitation of crystal hydrates and the one-sided growth of CSH. The simulations of the two effects must be achieved through hydration simulation. Herein, the cement particles placed in the simulation system are hydrated according to the status-oriented computer model developed by Ma and Li.^{37,38} Basic assumptions of the computer model are shown in Fig. 3.

In this model, the degree of hydration α is defined as the volume fraction of hydrated cement, or the volume of hydrated cement $V_{hydrated}$ over the original cement volume V_{cem}

$$\alpha = \frac{V_{hydrated}}{V_{cem}} \quad (5)$$

Hydrated cement changes to hydrates, and the volume expands by a factor κ_h , which represents the volume of hydrates created when a unit volume of cement is hydrated. To simulate the microstructure change following hydration, hydration fronts of all cement particles are assumed to penetrate at the same rate (in depth/step) inward to simulate the growth of inner hydration products, and all cement particles are expanded outward to simulate the growth of outer hydration products. Thus, at a specific status, the penetration depth for all particles is half d_{cor} as shown in Fig. 3. Particles smaller than d_{cor} have been totally hydrated while larger ones have not (still with an unhydrated core). As shown in Fig. 3, the inner product layers are believed to be somewhat condensed, while the outer product layers are loose due to the insufficient packing of hydrates in the original capillary space. Appropriately simplifying the simulation, the volume of small capillary pores that can be determined by nitrogen adsorption is added to the outer product layers, and large capillary pores are simulated by the remaining spaces outside the outer product layers. All of these descriptions are summarized as

$$V_{inner} = V_{hydrated} \quad (6)$$

$$V_{outer} = (\kappa_h - 1) \cdot V_{hydrated} \quad (7)$$

Fig. 3—Sketch of basic assumptions of status-oriented computer model for cement hydration simulation.

$$V_{outerlayer} = V_{outer} + V_{BJH} \quad (8)$$

$$V_{BJH} = \phi_{BJH} \cdot V_p \quad (9)$$

where V_{inner} and V_{outer} represent the volume of inner and outer products, respectively; and $V_{outerlayer}$ is the summation of the outer products and small capillary pores V_{BJH} , which equals the product of small capillary porosity ϕ_{BJH} determined by nitrogen adsorption and the volume of cement paste V_p . In simulations, given a degree of hydration, inner hydration product voxels are formed inward from the original boundaries, one layer by one layer, while outer product layer voxels are formed one layer by one layer contacting with the outer surfaces of the hydrated cement particles. When different outer product layers touch each other, only free surfaces are allowed to grow continuously in their outer-pointing normal directions. Newly formed voxels of different types are counted separately, and running stops once values calculated from Eq. (6) and (8) are fulfilled.

Using this computer model, the one-sided growth effect can be easily simulated. A modification is needed to take the nucleation and precipitation of crystal hydrates into consideration. For this purpose, the volume of crystal hydrates $V_{crystal}$, such as calcium hydroxide and ettringite, should be separated from that of the outer hydration products. The $V_{crystal}$, in this preliminary study, is simply assumed to be 40% of the volume of the outer hydration products V_{outer} . The other 60% is taken by the volume of outer CSH V_{OCSH} . Thus, when using the previously mentioned status-oriented computer model to simulate the evolution of ITZ, one should replace V_{outer} in Eq. (8) by V_{OCSH} and form the crystal grains separately. In each step, before the growth of outer product layers, the number of crystal phase voxels should be calculated first, then the number of nuclei is determined according to the principle used by Bishnoi and Scrivener³⁹ to decide

(a) The overall view

(b) Magnified area of ITZ overlapping

Fig. 4—Central cross-sectional view of simulation system after hydration. (Note: $w/c = 0.5$; $t_p = 80 \mu\text{m}$; age = 3 days; $\alpha = 0.56$.)

how many crystal particles will be formed. The locations of the nuclei are determined randomly based on probability. The probability is very low at the surface of hydrated cement particles, high in large capillary pores, and very high at aggregate surface in light of the theories introduced in the previous section, “Evolution mechanisms of ITZ.”^{8,9,11} The remaining crystal hydrate voxels are placed randomly to contact with these nuclei or earlier placed crystal hydrate voxels to form crystal hydrate particles. After that, the outer product layers containing outer CSH and small capillary pores are generated. Thus, some crystal hydrate particles may be either completely or partially embedded in these layers.

The central cross-sectional view of a hydrated system ($\alpha = 0.56$) corresponding to the one in Fig. 2 is shown in Fig. 4(a). In the grayscale images shown in Fig. 4, gray levels 0, 85, 100, 170, 200 and 255 represent a large capillary pore, outer product layer, aggregate particle, inner product layer, crystal hydrates phase, and unhydrated cement grain, respectively. Figure 4(b) is a locally magnified image in which the black rectangle indicates the example of bulk paste, while

Fig. 5—Example of porosity distribution curve generated by simulation.

the white rectangles indicate the overlapped ITZs. It is clear that the overlapping of ITZs results in highly porous regions under the filtration effect.

After hydration, volume fractions of more components can be computed by counting their voxel number using the method described in the previous section, and the corresponding distribution curves can be obtained. For the hydrated system, Eq. (4) needs to be modified to

$$\phi_i = \frac{N_i}{N_{\text{pore}} + N_{\text{uc}} + N_{\text{crystal}} + N_{\text{inner}} + N_{\text{outerlayer}}}, \quad (10)$$

$i \in \{\text{pore, uc, crystal, inner, outerlayer}\}$

where N_{crystal} , N_{inner} , and $N_{\text{outerlayer}}$ are the numbers of crystal hydrate voxels, inner product voxels and outer product layer voxels; and ϕ_i and N_i indicate the volume fraction and voxel number of one of the five phases in hydrated cement paste.

SIMULATION RESULTS

With the simulated system, the porosity and the unhydrated cement volume fraction, the volume fractions of hydration products after hydrated, and even some configuration-sensitive parameters^{15,23} as functions of distance to aggregate surface can be plotted and used to define the extent of ITZ. However, as the porosity is most significantly related to transport properties, it will be emphasized in the analysis of the simulation results.

An example of porosity distribution along the distance to aggregate surface is shown in Fig. 5. It is clearly shown in this figure that single sample curves may fluctuate across a wide range, but after averaging a number of single curves, the average curve is smooth. Only an average porosity distribution curve can be used to determine the extent of ITZ, as ITZ should be considered as a statistical concept. To determine the thickness of ITZ, different criteria have been used in the literature. According to Hu and Stroeven,¹⁵ ITZ thickness is a parameter to measure the distance from the aggregate surface to where the bulk value of porosity is achieved. By this criterion, ITZ thickness t_{ITZ} is determined as $30 \mu\text{m}$ for the case shown in Fig. 5. In another criterion, ITZ thick-

Fig. 6—Influence of aggregate particle size on porosity distribution curves.

ness was defined as the distance over which the porosity is greater by a factor of 10% than the bulk porosity.¹⁸ ITZ thickness t_{ITZ} is 10.6 μm for the case shown in Fig. 5, by this criterion. However, this criterion is not good, as the 10% is arbitrary. The third criterion defines ITZ thickness as the distance from the aggregate surface to where the porosity drops down to the overall average porosity of the whole paste. According to this definition, t_{ITZ} reduces to 14 μm for the case in Fig. 5. The average paste thickness in concrete is normally from little more than 50 μm to around 200 μm ,^{11,17,34} and when compared with this paste thickness, ITZ thickness should be doubled. Thus, large ITZ thickness values will make the terms “bulk” paste and ITZ lose their meanings. The most significant differences between ITZ and the bulk paste occur only in a narrow aureole (10 to 20 μm), which should be considered the real ITZ.^{11,17} Therefore, the third criterion is selected in this study, based on which the influences of several factors on ITZ thickness are discussed in the following sections.

Aggregate particle size

The influence of aggregate particle size on the porosity distribution curves is shown in Fig. 6. In the figure, OS represents the outer surface (large aggregate particle) in the simulation system. In Fig. 6, all of the porosity distribution curves for OS and aggregate particles with the diameter of 300 μm , 200 μm , and 100 μm are average curves from more than 20 individual simulations. These curves do not show any obvious difference, which implies that the influence of aggregate particle size on porosity distribution, and thus ITZ thickness, is negligible. Therefore, in a specific simulation system, averaging can be carried out on all porosity distribution curves of aggregates with different sizes to generate the overall average curve, as shown by the “Average” in Fig. 6. Such an average curve should be used to determine t_{ITZ} . In the case shown in Fig. 6, t_{ITZ} can be determined as 14 μm , which is a constant in the specific system rather than a function of aggregate particle size.

Some researchers believe that only ITZs around coarse aggregate particles influence properties of concrete significantly. However, Neville¹³ claimed that ITZ exists around not

Fig. 7—Influence of characteristic paste thickness on porosity distribution curves.

only the coarse aggregate but also the fine aggregate down to the smallest particle size. As reported by Puterman,⁴⁰ the interface between cement paste and air bubbles even down to a few microns still shows characteristics of ITZ. As shown by the simulation results, ITZ should exist around aggregate particles down to a very small size, with constant thickness in a specific system. This finding supports the generally used assumption that ITZ thickness is a constant in a concrete or mortar in calculations of the effective transport properties.^{41–44}

Characteristic paste thickness

According to Eq. (1), if the particle size distribution of an aggregate is fixed and its specific surface area is fixed too, then increasing the aggregate volume fraction will result in the decreasing of characteristic paste thickness; if the aggregate volume fraction is fixed, using finer aggregate will result in higher specific surface area and smaller paste thickness. Thus, influence of characteristic paste thickness also reflects the influences of aggregate volume fraction or fineness. The effect of characteristic paste thickness t_p on porosity distribution curves and ITZ thickness t_{ITZ} is shown in Fig. 7. In the investigation range, this effect is moderate, but the trend is clear: thicker cement paste corresponds to larger ITZ thickness. In Fig. 7, for simulation systems with t_p of 80 μm , 100 μm , and 120 μm , t_{ITZ} equals 12.4 μm , 13.6 μm , and 14.2 μm , respectively. In other words, lowering aggregate volume fraction or using coarser aggregate leads to thicker ITZ. Manchiryal and Neithalath⁴² reported that increasing the volume fraction of sand tends to decrease the overall conductivity of mortar. Besides the increased tortuosity, the reduced ITZ extent may also be taken into account when explaining such a phenomenon. Much more directly, Elsharief et al.¹⁴ found that using finer aggregate could reduce ITZ thickness if aggregate volume fraction is fixed.

Water-cement ratio (w/c)

Fixing t_p at 100 μm , the effect of w/c has been investigated using the simulation system and is shown in Fig. 8. Figure 8(a) indicates that the lower the w/c , the steeper the drop of porosity following the increasing distance to aggre-

Fig. 8—Influence of w/c on porosity distribution curves and ITZ thickness.

gate surface. As a result, lower w/c brings on smaller ITZ thickness. Under the condition that t_p equals $100 \mu\text{m}$, the quantitative relationship between t_{ITZ} and logarithmic w/c can be fitted by a linear function with quite a high correlation coefficient, as shown in Fig. 8(b). Although such quantitative relationships are rare, qualitative descriptions of the relation between w/c and ITZ, similar to that shown in Fig. 8, can be found in the literature.^{14,45-47}

It was reported that in mortar or concrete, the effective w/c of bulk paste is lower than the overall w/c , while that of ITZ is higher.¹¹ By analyzing the simulation results, this phenomenon can be quantitatively demonstrated. Take t_{ITZ} as the boundary, the ITZ part and bulk paste part of the porosity distribution curve shown in Fig. 8(a) can be averaged separately to calculate the porosities of ITZ and bulk paste. Then the effective w/c of ITZ and bulk paste can be calculated from their initial porosities. The calculation results are plotted in Fig. 9 against the overall w/c . It can be seen in Fig. 9(a) that, following the increasing of overall w/c , the increase of porosity in ITZ and the reduction of porosity in bulk paste relative to the overall average porosity are almost constant. Calculated from this point, as shown in Fig. 9(b),

Fig. 9—Porosity and effective w/c comparison of ITZ and bulk paste.

the increase of effective w/c in ITZ and the reduction in bulk paste become gradually larger following the increase of overall w/c . As reported by Scrivener et al.,¹¹ the effective bulk w/c of a concrete with overall w/c of 0.4 and a standard mortar with overall w/c of 0.45 are respectively around 0.35 and 0.38. Similarly, according to the simulation and calculation, the effective bulk w/c are 0.35 and 0.39 respectively when the overall w/c equals 0.4 and 0.45 in the specific case shown in Fig. 9(b).

Incorporation of finer binder particles

It is a widely used assumption that the ITZ thickness is approximately equal to the mean diameter of cement particles. Thus, finer cement or binder will result in thinner ITZ. As only one particle size distribution of cement is considered in this study, the influence of the fineness of the binder system is considered by incorporating much finer binder particles, such as silica fume. In a simulation, one silica fume particle can be modeled by one voxel as suggested by Bentz et al.⁴⁸ Based on the predefined silica fume replacement ratio, the volume fractions of cement and silica fume can be calculated. In a simulation system, after placing cement particles and digitization, pore voxels are randomly replaced by silica fume voxels until the volume fraction of

Fig. 10—Influence of finer binder particles on porosity distribution curves.

silica fume is achieved. The influence of silica fume on the porosity distribution curve is shown in Fig. 10, where “reference” represents a pure cement system, and the curve of “SF 10%” represents a binder system in which 10% of cement by weight is replaced by silica fume. The overall lower porosity of the silica fume-incorporated system is an inevitable result for a weight-based replacement, as the specific gravity of silica fume is much lower than cement. Also, the ITZ thickness t_{ITZ} is 11.2 μm for the silica fume-incorporated system, while it is 13.6 μm in the pure cement system as determined from Fig. 10. This is because silica fume can make the packing of solid particles in ITZ much more sufficient. This kind of effect has been proven by experiments reported in the literature.^{29,45}

Degree of hydration (or age)

In previous sections of this paper, the initial states of several simulation systems have been studied. However, in experiments—for example, using scanning electron microscopy¹⁰—ITZ in a material has to be observed at a specific age, or a specific degree of hydration ($\alpha > 0$). In this study, cement hydration is simulated using the method described in the section “Evolution of ITZ.” An example is given in Fig. 11, in which a simulation system with a w/c of 0.5, a characteristic paste thickness of 80 μm , and a degree of hydration of 0.56 is analyzed. The distribution curves of four components, including large capillary pore, crystal phase, CSH, and unhydrated cement, are shown. The volume fraction of CSH in Fig. 11 is the summation of inner products and outer product layers, say $\phi_{inner} + \phi_{outlayer}$ according to Eq. (10), corresponding to the volume fraction of CSH that can be distinguished experimentally using BSE (back-scattered scanning electron microscopy). ITZ thickness t_{ITZ} can be determined based on the overall average levels of different microstructural features, but the results are different. As shown in Fig. 11, based on porosity, t_{ITZ} is around 9 μm , but if based on unhydrated cement or hydration products, t_{ITZ} tends to be larger. This phenomenon was also noted by Scrivener et al.¹¹ based on experimental findings.

ITZ thicknesses at different degrees of hydration (α) determined by the overall average porosity are obtained and

Fig. 11—Volume fraction distributions of different components in hydrated system.

(a) Porosity distribution curves

(b) t_{ITZ} -age relationship

Fig. 12—Influence of degree of hydration (or age) on ITZ thickness.

Fig. 13—Evolution of ITZ porosity and bulk porosity.

compared. The changing of the porosity distribution curve following α is illustrated in Fig. 12(a). It is obvious that the higher the α , the steeper the drop of the curve and the thinner the ITZ. The values of α , as input factors of the simulations, were experimentally determined from cement paste cured in water under an ambient temperature. For instance, in the case of paste with a w/c of 0.5, values of 0.36, 0.56, 0.67, 0.73, 0.79 and 0.81 for α correspond to the ages 1, 3, 7, 28, 60 and 120 days, respectively. By employing this relationship, the t_{ITZ} - α relation can be easily transferred to the t_{ITZ} -age relation. Following an increase in age, ITZ thickness decreases. The t_{ITZ} -age relationship can be fitted by a linear function under a logarithmic time scale as shown in Fig. 12(b). The average porosities of ITZ and bulk paste are plotted against the degree of hydration, as shown in Fig. 13. It is found that the difference between ITZ porosity and bulk porosity decreases with the hydration process and almost keeps constant at mature ages. This is consistent with experimental findings.¹¹

DISCUSSION

According to the simulation results, ITZ thickness is a function of paste thickness, w/c , binder fineness, and degree of hydration (or age), and varies from several microns to the mean particle size of cement. The values of ITZ thickness reported in the literature vary from several to over 50 μm , and most generally 10–50 μm .^{1–4,49} The large values should be attributed to two reasons. First, to study ITZ, researchers usually cast cement paste against glass or stone in the shapes of slab, cylindrical core, or tube instead of observing ITZ in real concrete. These model concrete specimens produce different ITZs from that of real concrete because they ignore so many details^{11,49} and generate most of the large values of ITZ thickness in the literature.^{1–4} Second, the sectional approach for ITZ characterization in real concrete overestimates ITZ thickness, as analyzed by Chen et al.⁵⁰ Thus, as indicated by Scrivener et al.,¹¹ the narrow aureole (10 to 20 μm) around an aggregate where the most significant differences between ITZ and bulk paste occur should be considered the real ITZ.

Fig. 14—Central cross-sectional view of simulation system with arbitrary degree of flocculation. (Note: $w/c = 0.5$, $t_p = 100 \mu\text{m}$.)

Even so, the values of ITZ thickness according to simulations presented in this and other works still seem to be smaller. Some modelers attribute such a phenomenon to the discarding of large cement particles due to the limited size of the simulation space.^{24,25,47} However, in the present study, the simulation space is so large that no discarding is necessary. The disregard of cement flocculation may be a reason for the smaller simulated ITZ thickness. However, flocculation can be considered in the simulation by introducing a probability based algorithm. If it is assumed that the flocculation probability of a cement particle is inversely proportional to its diameter, when generated a cement particle can stand separately or contacting with the earlier generated particles based on probabilities. In this way, an arbitrarily (not severely) flocculated system has been simulated as shown in Fig. 14. Compared with Fig. 2, it can be seen that the flocculation of cement particles leads to the appearance of larger capillary pores and results in a more significant difference between ITZ and the bulk paste, but only slightly increases ITZ thickness (13.7 μm versus 13.6 μm), according to Fig. 15. Another important thing is that bleeding is not considered in the simulations. This is not a big problem for simulating high-performance concrete, such as SCC, in which bleeding can be effectively controlled.²⁹ However, for normal concrete, bleeding is not negligible. Normally, researchers may believe that most of the bleeding water is cumulated below large aggregate particles, but after a comprehensive study on the microstructure of concrete, Crumie⁴⁹ stated that the microstructure differences between the top, side, and bottom of an aggregate are insignificant. This presents a possible way to consider bleeding in the simulations of ITZ; that is, treating bleeding water as water films with constant thickness, as calculated from the bleeding ratio, around aggregate particles.

Fig. 15—Comparison of porosity distribution curves of perfectly dispersed system and arbitrarily flocculated system.

CONCLUSIONS

A multi-aggregate approach has been proposed to simulate the formation of ITZ in concrete. In light of a modified status-oriented computer model, cement hydration in the simulation system and the evolution of ITZ have also been simulated. The proposed method has been successfully employed to reveal the influences of several factors on the characteristics of ITZ. Through preliminary simulations, the following conclusions can be drawn:

1. Decrease of the characteristic paste thickness, achieved by using finer aggregate or increasing aggregate volume fraction, results in smaller ITZ thickness.
2. Using a lower w/c can effectively reduce ITZ thickness. Increasing the overall w/c makes the increase of an effective w/c in ITZ and the reduction in bulk paste larger, which makes the difference between ITZ and bulk paste more significant.
3. Partially replacing cement with finer particles, such as silica fume, makes the binder system finer, results in more sufficient packing, and reduces the thickness of ITZ.
4. When the system is hydrated to a specific degree, several microstructural features can be used to define ITZ, such as porosity and the volume fractions of hydration products. However, the value of ITZ thickness depends on the feature used to define it.
5. ITZ thickness decreases with the increase of age (or degree of hydration). The difference in porosity between ITZ and bulk paste keeps constant at mature ages.
6. Flocculation of cement particles tends to increase ITZ thickness and the porosity difference between ITZ and bulk paste.

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