The interfacial transition zone in concrete; experiment versus computer simulation

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Abstract

Interfacial transition zones (ITZ) between aggregate particles and bulk paste play a major role in short-term and long-term behaviour of cementitious composites. Ample experimental data, obtained by different methods and measuring different features, do not offer a coherent perspective on the ITZ, unfortunately. The 'realistic' computer-simulation approach presented provides at least a qualitative basis for interpretation of the various experimental data depending on their configuration-sensitivity. Sources for differences between experiment and simulation are discussed.

1 Introduction

Cementitious materials can be considered consisting of particulate elements on the various levels of the microstructure. Particularly relevant for physico-mechanical properties is the packing of the binder particles on micro-level in the fresh concrete. This so-called matrix stabilises after hydration the skeleton of the densely packed aggregate particle on meso-level. The binder particles pack differently in the pockets between the aggregate particles (in 'bulk') and near their surfaces, in the ITZ. Hence, the starting situation in the ITZ at the onset of hydration deviates from that in bulk. The initial packing gradients over the ITZ's thickness can be expected, therefore, also offering valuable information for the hardened state, as was shown earlier [1-3]. Research data reveal the ITZ to be generally more porous and having a lower strength [4-6]. Hence, the ITZ is of paramount importance in studying short-term as well as long-term properties of cementitious materials. For an excellent survey of the methodological aspects of studying the ITZ, and a wide range of experimental data, see [6]. This paper will concentrate on the computer-simulation framework and refer to such experimental data.
Commonly, the average volume fraction of particles (or: phases) at a certain distance from the interface is determined, offering information on the density or porosity gradient over the ITZ. This is a measure for structural composition. When obtained by high-resolution methods like (electron) microscopy or X-ray diffraction, a relatively thin interface layer is found (say, 20-40 μm). A low-resolution approach to detecting composition gradients is by micro-hardness measurements [7]. The averaging effect of the indenter head inevitably leads to a more extended interface layer, of, say, 100 μm. Some properties will depend on group behaviour of hydrating cement particles. As an example, the amount of unhydrated cement after hydration will be governed by the distance distribution of particles (availability of water during hydrating!). Hence, here we are confronted with a configuration parameter of the fresh cement paste [8]. Configuration deals with the spatial arrangement of particles in a group [8]. For configuration homogeneity a considerable larger material volume is necessary than for composition homogeneity [9]. This points towards a more extensive ITZ when configuration parameter is measured. As a consequence, the published experimental data reveal the ITZ thickness to fluctuate between wide boundaries. The computer-simulation approach could offer the proper framework for interpretation of experimental data in terms of configuration-sensitivity of the experimental parameter and of possible biases in sampling strategies.

2 Static simulation of particle positions

Simulation by computer of the particulate structure of the ITZ in cementitious materials can at least qualitatively reveal the effects of technological parameters and of sampling strategies on the extension and structural features of the ITZ. The most common approach to this problem is by the so-called sequential random generator based systems (RG). It is referred to as a static simulation process. It involves locating the particles (generally spheres) sequentially inside a container. Each location is governed by randomly generated co-ordinates. 'Overlap' with earlier generated particles will result in rejection, whereupon the generation process is continued. The number of rejections will increase dramatically at high volume fractions, making the generation process very time-consuming, if not impossible at all in the highest density range. Simulation of a multi-size particle composite requires starting with the largest particles in the mix. The system obviously excludes the mechanism of mutual particle interaction, which is so characteristic for the production stage of cementitious materials. The re-generation after rejection inevitably leads to an under-estimation of a natural phenomenon as particle clustering [10]. The generated nearest neighbour distribution of the particles will reveal, as a consequence, dramatically large biases at higher particle densities [10]. Three of the more popular systems in this category were developed by Roelfstra [11], by Diekkämper [12], and at NIST [13].
3 Dynamic simulation of particle positions

The SPACE (Software Package for the Assessment of Compositional Evolution) system is based on a dynamic concept of simulating the production process of composite materials, i.e., in case of concrete: mixing of aggregates and paste, or cement and water. The details of the generation system have been published by the authors elsewhere [1,2,14]. To be able to simulate effects such as clustering and to reach high volume densities, element motion and inter-element collision are modelled, leading to effective ingredient mixing. This stage is referred to as the dynamic stage.

The general simulation concept can be described as follows:

- Initially, a structured or random 3-D dilute distribution of elements with pre-defined shape and size distribution (such as the grading curve) is generated within the boundaries of a container. So far, only spherical particles can be conceived by SPACE. This stage can be similar to that of a random generator based system. Next, random linear and rotational velocity vectors are assigned to each element.

- The second step, the actual dynamic stage, is an iterative procedure where location and orientation of all elements are changed at each time step according to a Newtonian motion model. This motion model relates the element's linear and angular displacement to a set of conditions enforced on the element (e.g., gravity, friction, etc.). When elements meet during this time interval, a contact model defines the effect of contact on the motion/rotation update. Inter-particle influences – one of the requirements for achieving a more versatile system – are incorporated in the contact model. Additionally, electrical or chemical inter-particle forces may be added to the motion model. This will allow to more accurately adjust SPACE simulations to the particle aggregation conditions (i.e. flocculation) of the fresh cement paste. In the present concept, the use of this facility was considered to needless complicate matters, because no quantitative estimation of the ITZ thickness was pursued. The density can be varied during this stage by changing the size of the container (compacting the structure), or by applying a gravitational force.

- Finally, the iteration stops when certain conditions are reached, such as the relevant volume fraction of aggregate, or the required water to cement ratio.

The final distribution state can incorporate effects due to gravity and to inter-particle influences. Simple physical laws may be used to define the inter-particle relationships, by introducing parameters such as specific mass and energy dissipation. Maximum packing densities can easily be simulated by the SPACE system. Such densities are relevant for aggregate packing problems on engineering level, or for binder particle packing problems particularly at low water to cement ratios, appropriate for High Strength or High Performance Concrete systems.
4 Composition of particle packing near interfaces

The ITZ is commonly modelled as a shell-like structure around the particles of the aggregate [4]. The properties of the shell are only a function of the distance to the interface surface. In an oblique direction, the properties should be seen as representing the average of the natural variation occurring in cementitious materials. This average value is derived in the computer-simulation approach from a field of 100x100µm, being the cross section parallel to the external surface of a container with linear dimensions of 100µm. Graphs presented in this paper are the average of six simulations. Fig. 1 presents examples of the technological impact of the major upgrading

![Figure 1: Effect of w/c of the model (PCA) cement paste (top), and of fineness of the cement (PCA and PCC) at w/c=0.2 (bottom) on volume density of the paste as function of distance to the interface.](image-url)
mechanisms in concrete technology on the volume density gradient over the ITZ. We see that the thickness of the ITZ is diminished by a factor of about 2 upon reducing the water to cement ratio, w/c, from 0.5 to 0.2. At w/c=0.2, Fig. 1 reveals the moderate influence of cement fineness on the ITZ's thickness. Note that the real PCA and PCC have Blaine numbers of 1760 and 2660 cm²/g. Additionally, these pictures present evidence of the favourable effects of these upgrading mechanisms on volumetric density in the immediate neighbourhood of the aggregate particle's surface. This can be also expressed in a reduction in porosity. In the simulation study, computing time limits required the particle size range to be restrict to 1.9 to 45µm. A maximum of 10,000 spherical cement grains were dispersed in a cubic container with 100µm linear dimensions. The particle size distribution function of the model cements is made to closely match the Rosin Rammler curve, \( G_d = 1 - \exp(-bd^3) \), \( n \) and \( b \) being constants with values \( n=1.3 \) and \( b=0.0175 \) for PCA and \( n=1.4 \) and \( b=0.033 \) for PCC [1,15].

These trends in the effects of these major technological parameters on the ITZ thickness are supported by experimental evidence [4-7]. In such experiments, the common measuring parameter in quantitative image analysis approaches is porosity, which is the inverse of volumetric density. Also indirectly and only in an approximate way, micro-hardness observations can be interpreted as revealing changes of volumetric density over the ITZ, whereby account should be given to the averaging effect due to the dimensions of the indenter. The relevant curves show the same features as observed by computer simulation. Based on such SPACE simulations and succeeding hydration it was found that maturity had reversed effects on normal and on HP concretes: at low water cement ratios (w/c=0.2), the ITZ thickness declined somewhat with maturity, whereas an increase was detected for normal concrete (w/c=0.5) [1].

5 Configuration of particle packing near interfaces

The SPACE system has demonstrated the occurrence of size segregation at interfaces. As shown earlier [2], the maximum in the number of particles per unit of volume (\( N'V = \text{'number density'} \)) of a certain size range of particles is proportional to the (average) size of such particles. One practical implication is that mineral admixture particles smaller than those of the cement will concentrate at the interface, thereby increasing local volume density and reducing particle spacing (and improving physical bond capacity). The SPACE system 'realistically' simulates nearest neighbour distances, and thus also distances between particles and an interface. Interparticle bond depends on particle spacing, and thus on the fineness of the binder at a certain volume fraction. Supposedly, a global interparticle physical bond capacity could be associated with \( \lambda^{-3} \) [10], where \( \lambda \) is the mean free path. The mean free path is the average of all unobstructed surface-to-surface distances to
neighbouring particles [16], whereby $\lambda = 4(V_p/\pi)/S_p$, with $S_p$ as the specific surface area of the particles. The total perimeter length of the circular cross-sections of the particles per unit of area in the section plane, $L_4$, is related to the surface area per unit of volume by $S_p = \frac{4}{\pi} L_4$. This allows for an unbiased and exact estimation of $\lambda$.

Fig. 2 presents simulations of Rosin-Rammler mixtures of a maximum of 10,000 grains with sizes between 1.9 and 45\mu m, which were dispersed in a cubic container with linear dimensions of 100\mu m. It can be observed that the 'global bond capacity' disproportional increases at closer distances to the interface with declining water cement ratios. This effect is strongest for the finer-grained cement. Hence, the impact of upgrading concrete by a

![Figure 2: Parameter proportional to global bond capacity for different water to cement ratios of PCA (top) and PCC (bottom) as function of distance to the interface. $\lambda$=mean free spacing in \mu m.](image)

reduction in water to cement ratio and taking a finer cement, or eventually by adding a finer mineral admixture, becomes apparent from these two figures. Particularly the zone close to the interface surface, which is for normal concretes the weakest link in the mechanical system is disproportionate strengthened. A remarkable observation is further, that contrary to the effect on composition, the chosen configuration parameter leads to an increase in ITZ thickness at a reduced water to cement ratio! What we see further is that the quantitative effect of technological changes is far more pronounced in the configuration case. The thickness of the ITZ seems to increase in the latter over the range of water cement ratios by about a factor of 6 to equal maximum grain size of the model cement for a water to cement ratio of 0.2. In the composition case, a factor of 2 is involved with a maximum extension of about half the maximum grain size at the highest water to cement ratio. Available experimental data reveal similar features.

6 Experiment versus computer-simulation

When microscopy is applied to randomly selected ITZs in polished sections or in thin section projections of real concretes, observations on gradients (and thus on the extent of the ITZ) will inevitably be biased, too, although this is not quantitatively accounted for in the evaluation [4]. This bias in outcomes of random and systematic (serial) sectioning is derived elsewhere [17]. It demonstrates observations on the ITZ thickness on average about 50% too high (not just 'somewhat higher' as accepted in experimental design [4,6]). To quantitatively bridge the gap between experimental data and the presented simulation results, account should be given to the larger size range of real cements. This will exert a direct effect on the ITZ's extent. For the sake of the argument, proportionality is therefore assumed between the ITZ's thickness and the maximum grain size of the real cement. For a cement with a noticeable fraction of grains in the 80 to 100μm size range, this would lead to a 20 to 30μm thick ITZ shell for composition, and a 80 to 100μm one for configuration for water to cement ratios of 0.5 or lower. On the other hand, experimental data on the ITZ's thickness may reflect other mechanisms than 'packing' such as interface bleeding, and cracking.

The common approach nowadays is by delineating strips of 5 to 10μm width parallel to the aggregate particle's surface in the BSE image [4,7]. These strips with a length of about 250μm are subjected to (automatic) quantitative image analysis. A pre-requisite is mostly that the contrast in the image is enhanced by subjecting it to pattern recognition algorithms. This inevitably leads to extra scatter and even biases. A large number (20) of 'similar' samples are used to get reliable averages [4]. Nevertheless, the number of samples should be a function of the degree of configuration-sensitivity of the measuring parameter to arrive at a similar sensitivity level. In the present computer simulated set up, 6 images of 100x100μm were
analysed. Herein, the spatial distribution of all particles of the *model cement* is known (with respect to the co-ordinates and associated radius of each particle), so structural 3-D information attributed in the SPACE system to a section does not suffer from such inevitable experimental 'uncertainties'. yet, total area scanned in the latter case is 2.4 times that of the experimental approach. Sensitivity of the computer-simulation approach is exceeding that of the general experimental one. Moreover, a major difference between the two is that the images scanned in the computer simulated case are *parallel to* the aggregate particle's surface averaging over the natural structural variation in the 'shell', whereas the experimental one is relying on a narrow strip of which the width is in plane with the structural gradient.

A fundamental problem is that the ITZ has no obvious boundaries (Figs. 1-2). Determination of the ITZ's thickness from experimental or simulated gradient measurements can therefore be neither accurate nor objective. From the present comparison the major conclusion can be drawn that the extent of the ITZ will depend on *material composition, as well as on the degree of configuration-sensitivity of the parameter at issue*. Since structural scatter in case of configuration can be one order of magnitude larger than in case of composition [9], particularly the configuration-sensitive parameters measured experimentally (such as the amount of anhydrous cement) will be camouflaged by structural scatter, leading to biased estimates (too small) of the ITZ's extension, see Fig. 3. This makes comparison with similar observations by the SPACE system impossible. For SPACE explorations of the hardened state, see [1-3].

![Graph](image)

Figure 3: Area % of unhydrated cement in 10μm wide strips of ITZ [4].
7 Conclusions

The presented 3-D structural simulation system is versatile and able to generate particulate systems of different nature. In this paper, it has been applied to packing problems in the ITZ. It presents realistic estimates of structural parameters, which can not always be obtained experimentally or sometimes only at great efforts. In agreement with experimental data, the ITZ's extent was found reduced at lower w/c ratio of the paste, and at larger fineness of the cement. The effect of such technological parameters on the ITZ's extent is only moderate, however. Interparticle bond capacity in the ITZ, and in analogy interface bond capacity, were demonstrated to be significantly promoted by larger fineness of the cement and by a reduced w/c ratio. The associated ITZ's thickness increases significantly at the lowest w/c ratio.

The extent of the ITZ was found to depend on the parameter observed, as also observed experimentally. This is shown being due to the different degrees of structural-sensitivity involved. Since the ITZ has no distinct boundaries, deriving its thickness for a given material composition from gradient structural information, the would be equally difficult for experimental and simulated data, provided a similar sensitivity level can be achieved in the experimental set up. This is generally not the case, however. The advantage of the simulated approach is that fields can be analysed parallel to the aggregate particle's surface, whereas the experimental approach should rely on narrow strips in the direction of the gradient structure. The structure of the ITZ shells in the real material and in the simulated one are revealing 'natural' scatter in the shell at a constant distance from the surface. This variation is larger the larger the dependence of the measured parameter on group behaviour. Hence, the sample size should be considerably enlarged in case of configuration-sensitivity, which is not the practice in experimental approaches, but can easily be accommodated in the computer-simulation concept.

References

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