Interfacial transition zone in concrete: its relevance for engineering applications

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This paper discusses the characteristics of the interfacial transition zone (ITZ) relevant for engineering applications of concrete structures, in particular for permeability. Basis is the particulate nature at meso- and microlevel. The existence of the ITZ, its characteristics as to pore network development and to the resulting permeability are evaluated and illustrated by data obtained on DEM-based virtual cement paste. ITZ contributions to permeability are shown higher than from bulk. However, in research as well as under practical engineering conditions of the concrete, the material is not fully saturated as generally assumed and required for the derivation of permeability data from information on the pore network structure. The paper demonstrates that the relative prominence of the ITZ contributions to permeability are lost under such conditions. Hence, the general conclusion is that the ITZ is a real phenomenon, however gradient structures of various parameters will dramatically fluctuate on this low level of the particulate structure. For interpretation of this behaviour, the representative volume elements for structure-insensitive and -sensitive properties are introduced. Though, scientifically of interest, the actual engineering conditions lead to similar bulk and ITZ contributions to permeability.

Key words: Cement, concrete, discrete element modelling (DEM), interfacial transition zone, packing, permeability, representative volume element, pore saturation

1 Introduction

Concrete is a building material that derives its resistance to loading from a wide size range of hard densely-packed aggregate particles, bound together by a wide size range of cement particles that after hydration fill out most of the empty places left by the aggregate grains. Certainly, a major scale difference can be observed between these two packed particle systems. However, long-established knowledge on packing phenomena are applicable on both levels of the material structure.

This paper does not aim systematically reviewing the relevant studies of particle packing, a major part of which is outside the concrete technology field. We will merely select those observations that are relevant for explaining the shifting ideas on the Interfacial Transition Zone (ITZ) in concrete technology. This may elucidate its features and its possible engineering impact, which is basically concrete's permeability. Concrete's major resistance to (compressive) loadings is unfortunately over the years suffering from gradual degradation of the material. This is due to (polluted) water that can transect the material through the pore system, which inevitably develops during the hydration process. Degradation can be due to aggressive agents in the water or be the result of the freeze-thawing mechanism.

The pore system is, of course, directly governed by particle packing characteristics. The concrete near the mould is known to differ from bulk material as a result of particle packing phenomena (the so-called wall effect). In a completely analogous way will the fresh cement packing near the aggregate grain surfaces differ from that in bulk as a result of cement particle packing characteristics (Ollivier, *et al.*,1995; Scrivener, *et al.*, 2004). The less efficient packing near the aggregate surfaces is generally reported resulting after hydration into a higher porosity. This supposedly more porous zones around aggregate grains are referred to as the ITZs. Particle packing characteristics and resulting effects on material structure (like porosity) will reveal a gradient over this boundary zone that merges into bulk properties at its inner "border".

This is all established knowledge and supported by experimental evidence. The paper will argue on the basis of its particle packing nature that the ITZ cannot be so clearly defined as may be concluded from the afore-mentioned logic information. This has to do with structural variation, or *inhomogeneity*. An issue that will be elaborated later. This is a crucial issue, because it explains that gradient structures cannot easily be measured. Experimentalist have been drawing earlier the conclusion from disparity between expected characteristics and failing experimental efforts to reveal these characteristics that the ITZ did not exist (Diamond and Huang, 1998). Yet, it exists and the underlying arguments for explaining this are equally powerful for predicting its relevance (*e.g.*, for permeability of concrete), as we will demonstrate.

Nowadays, we are able simulating in 3D the hardened cement paste between aggregate grains in the computer. This virtual material can be called "compupaste" (in analogy with earlier defined “compucrete”). To get proper information on relevant material properties, the simulation should be as realistic as possible. It must be obvious that at the particle packing densities met in practice, the dispersion of the aggregate or cement particles should be between *chaos* (complete randomness) and *order*. This seems trivial because Einstein mentioned already that complete randomness can exist only below volume percentages of 2 to 3 (Stroeven, *et al.*, 2008). And fully packed concrete in a state of order is irrelevant, of course. So, discrete element modelling (DEM) is the proper answer (Li and Stroeven, 2018). The compupaste made this way renders possible investigating the characteristics of the pore network structure.

It has been anticipated occasionally in the literature that the ITZ would play a dominant role in transporting a fluid through the material due to its relatively higher porosity. If so, concrete’s packing density would be important to stimulate ITZs overlapping, promoting permeability. However, also contradictory experimental evidence can be found in the relevant literature (Diamond and Huang, 1998; Shane, *et al.*, 2000; Maghsoodi and Ramezanianpour, 2012; Diamond, 2003). This is relatively irrelevant for reaching our goals; hence, we will not scan the literature on this issue. The aforementioned assumption can be proven incorrect, reducing the relevance of the ITZ for concrete permeability properties. In fact, continuous pores are found meandering through the cementitious material pocketed between aggregate grains. This also involve pores that originate from or transect the ITZ. Hence, particle packing characteristics (inhomogeneity) will also here provide the answer to the “why not”, as we will discuss later.

Things are even more complicated as more recent studies demonstrate. Pores are never empty or completely filled up by the fluid in engineering practice. Even in research where fully saturated material is supposed to underlie the analytical evaluation, this is proven not the case. It was recently demonstrated that in partly saturated conditions the relevance of the ITZ for concrete permeability is further reduced. This will explicitly be demonstrated. Hence, the ITZ exists for concrete researchers. However, for practicing engineers, the ITZ is not of great significance under practical conditions of the concrete. Presenting the supporting evidence for this statement is the goal of this paper. Of course, the relative impact of the ITZ on permeability has to be reviewed when confronted with extreme climatic conditions. However, this can be realistically simulated with compupaste.

2 Particle packing

As stated earlier, the discussion on the very existence of the ITZ starts with the particle packing phenomenon. Additionally, it governs the formation of pore network in which individual pores may de-percolate during progressing hydration of the cement particles. This depercolation process is also strongly depending on the particle distribution characteristics: particle packing *pur sang*.

This paper does not aim referring to leading papers on particle packing, many of which are outside the concrete technology field. We are interested here in discussing generally accepted findings relevant for the posed problem. A first relevant case would be explaining the packing differences in bulk and in the boundary zone, whether dealing with concrete aggregate or fresh cement particles. On both levels of the material structure, it is acknowledged that a particle is not free to find its "natural" place near a rigid surface. Freedom of such a particle is restricted by its size. The largest particle has its centre forced to stay the particle's radius away from the rigid surface. As a result, finer particles are stimulated to fill up the positions closer to the rigid surface. Hence, the particle size distribution will reveal a gradient upon approach of this rigid surface (Ollivier, *et al.*, 1995).

Reformulated into more scientific terms, the latter statement says that the weight (or amount)) of particles of a certain size in a representative volume element (RVE) for *weight* reveals a gradient in the boundary zone. For the same size of RVE for this *structure-insensitive property* "weight", the bulk values of similarly-sized particles will be approximately constant. It is generally accepted that the linear dimensions of this RVE exceeds particle size by a factor of, say, 5 (Cook and Seddon, 1956; Stroeven, 1973). Of course, the gradient structure in the boundary zone is different for each particle size (range). Still, this does not say anything about the *distribution* of the (range of) particles!

To characterize this distribution, generally spacing parameters are used. Yet, we are not focussing on details of the different spacing factors; we merely want to stipulate that there are *structure-sensitive* parameters that with different degrees of structure-sensitivity reflect particle dispersion. And structure-sensitivity is at the basis of pore formation and depercolation at increasing hydration time. This effect of structure-sensitivity is shown in Figure 1. At the left, a comparison between DEM-based virtual cement paste (produced by SPACE/HADES systems) - which closely simulates production conditions - and random sequential addition (RSA)-based material (produced by HYMOSTRUC (van Breugel, 1995)) – with a higher degree of *order* in particle dispersion. Due to the more even distribution in the latter case, pore de-percolation starts later and proceeds very fast (pores have about the same size). At the right, the method based on a random particle distribution system (state of *chaos*) that leads to a too gradual pore depercolation process. Hence, independent on

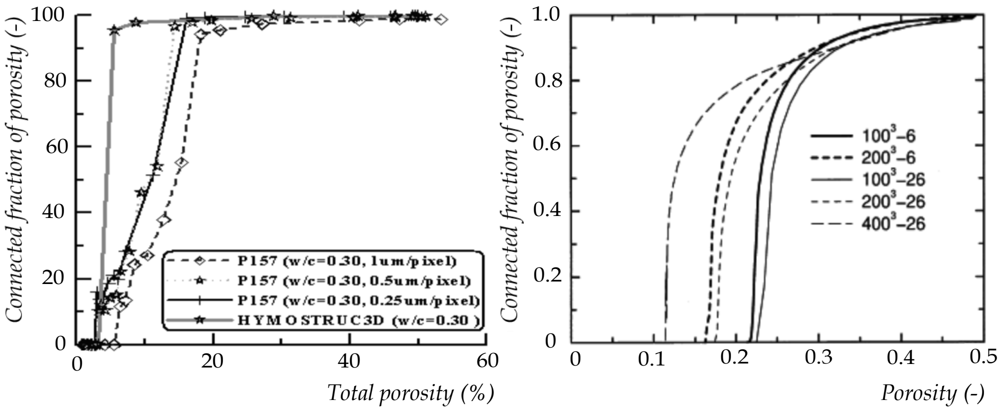

Figure 1. Evolution of pore de-percolation during hydration versus porosity for model cement pastes (w/c = 0.3) of which the fresh states were generated, at the left by HYMOSTRUC3D and by DEM system SPACE (Li and Stroeven, 2018), and at the right according to Garboczi and Bentz, 2001). Influence of resolution is also depicted (100^3, 200^3 and 400^3 correspond to a resolution of 1, 0.5 and 0.25 µm/pixel, respectively).

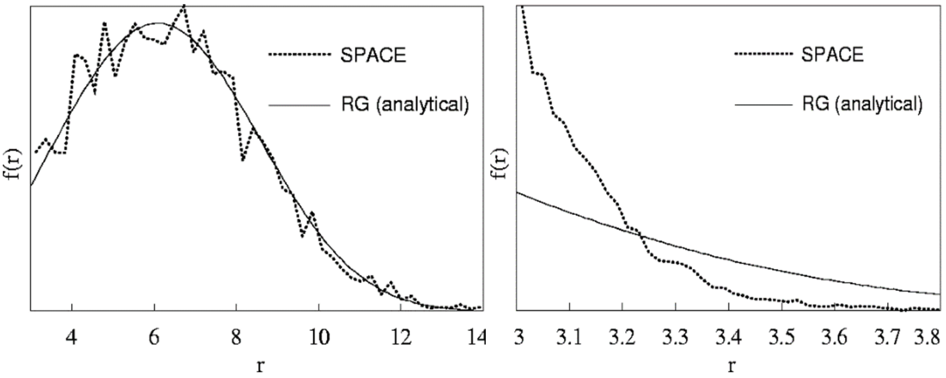

Figure 2. Deviations between predictions on nearest neighbour density distributions, f(r), at 1% (left) and 30% (right) by volume of aggregate obtained by a random generator (RG) (RSA algorithm), respectively, and by a concurrent algorithm based (DEM system SPACE) computer simulation system (Stroeven, 1999)

used sensitivities, DEM reflects reality more closely and will produce superior results. Figure 2 (right) also reveals simulations by DEM remote from RSA estimates for particle packing densities in engineering practice.

Acknowledging that structure-sensitivity is of practical engineering relevance, we have to state here that the size of the relevant RVE is significantly exceeding that for structure-insensitivity. Depending on the type of spacing parameter, this can involve a factor of, say 5 to 10 (Stroeven, 1973; Hu, *et al.*, 2005). Moreover, distribution of structure-insensitive parameters is Gaussian (normal distribution), while this is Poisson-like (skew distribution) in case of structure-sensitive properties, as demonstrated in Figures 2 and 3.

3 Structural characterization of the ITZ

With an average cement particle size of 15 µm, the linear size of the structure-insensitive RVE will be about 75 µm. But that of a structure-sensitive RVE could amount to 500 µm. We are not interested here in the exact estimation of these sizes; however, we can see that the linear dimension of the RVE for a structure-sensitive property (such as particle spacing) will exceed the linear extension of the ITZ (in the literature frequently referred to as 50 µm) by an order of magnitude. This has far-ranging consequences. The most obvious is that experimental measurements in radial direction of the ITZ bordering an aggregate

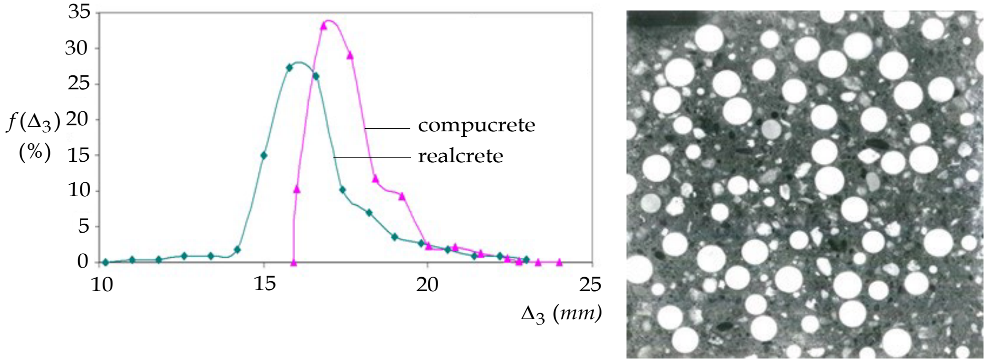

Figure 3. (left) Frequency distributions of the nearest neighbour, Δ_3, among 16 mm ceramic spheres in a 200 mm sample of "realcrete" (sawn from 250 mm sample - see Fig. 3 right) and "compucrete" (computer-made concrete). respectively. Differences are mainly due to sawing inaccuracies for serial sectioning of the realcrete (Stroeven, 1973).

grain will be scattering far too much to find relevant gradient information. Seemingly, the ITZ does not exist.

The solution is, of course, to extend the measuring area along a strip at constant distance to the aggregate grain surface and to average observations. This is very cumbersome for experimental approaches. It can be easily realized in virtual situations leading to the results presented in Figure 4. More specifically, they were obtained on virtual cement paste produced with the HADES system (dynamic DEM). (Le, *et al.*, 2012; Stroeven and Stroeven, 2001). *The ITZ is apparent, so, existing*!

In the framework of pore structure exploration, random points are distributed in the virtual hardened cement paste produced in cube space by HADES. The cube is provided with two rigid surfaces of, supposedly, aggregate grains (at the left and right). Figure 5 presents the points dispersed in pore space. The existence of the ITZ is apparent. Of course, the point fraction in pore space equals porosity.

4 Interfacial transition zone and porosity

Task is here to explain the background of Figure 4. Hence, how to assess by a virtual approach a realistic representation of the pore network structure in hydrated cement paste.

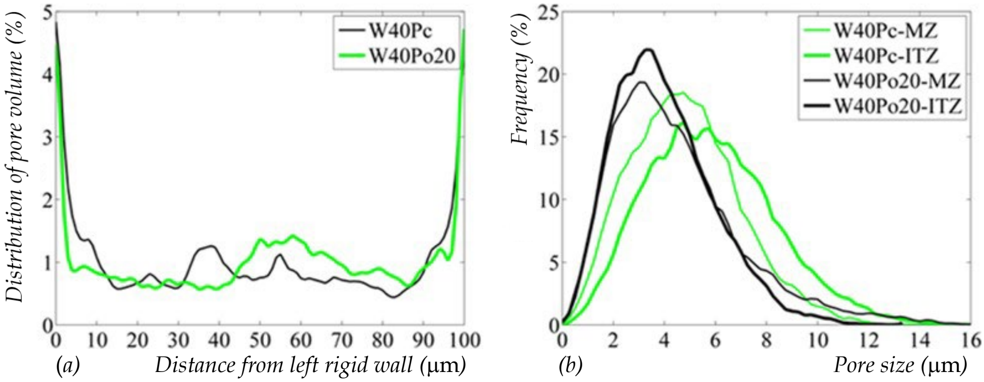

Figure 4. (a) Gradient structures of total porosity in plain and blended cement paste between neighbouring aggregate surfaces. (b) Pore (throat) sizes are larger inside the ITZ zone in the PC, however are disproportionately refined by blending. MZ is middle zone between the ITZs; Pc = Portland Cement; Po20 is PC with 20% RHA; W40 = w/b or w/c = 0.40. Results produced by HADES.

The simulation process starts by DEM packing of the original cement particles, in the present case assumed spherical (Fig. 6).

The next module involved in the system is hydration simulation by XIPKM method. This is an eXtended version of the conventional IPKM method (Le, 2015; Le, *et al.*, 2013; Navi and Pignat, 1996). The hydration process reduces the space between the packed cement particles. Hence, gradually a pore network structure is formed of which pores may de-percolate as a result of progressing hydration, as demonstrated in Figure 1. To characterize the resulting pore network structure, a robotics concept is applied to the situated material. It is referred to as DRaMuTS (Double Random Multiple Tree Structuring) (Stroeven, *et al.*, 2012). Figure 7 at the left depicts all pores in the simulated hydrated cement paste. The dead-end pores and isolated ones are thereupon removed and the continuous channels between top and bottom surface of the specimen are resulting. Mind that the left and right sides of the cube are rigid, so ITZ's will have formed. However, visual observations of the right picture do not reveal pore channels to follow the ITZ. Hence, so far we have stated that the ITZ is real and that its porosity is higher than in bulk (Figures 4 and 5).

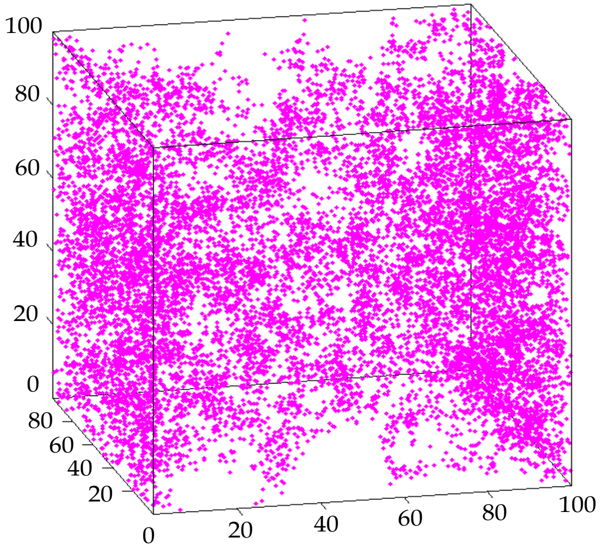

Figure 5. Example of UR dispersed points in pore space of two months hydrated PC with w/c = 0.2 in 100 μm cube; total porosity is 13.6% and connected fraction is 95.3%. The higher porosity in ITZs adjacent to the rigid (aggregate) surfaces (left and right) is obvious (Le, et al., 2013).

Nevertheless, large structural variation on microscale leads to pores meandering through bulk space (Fig. 7). As a consequence, the relevance of the ITZ *for pore structure development seems restricted.*

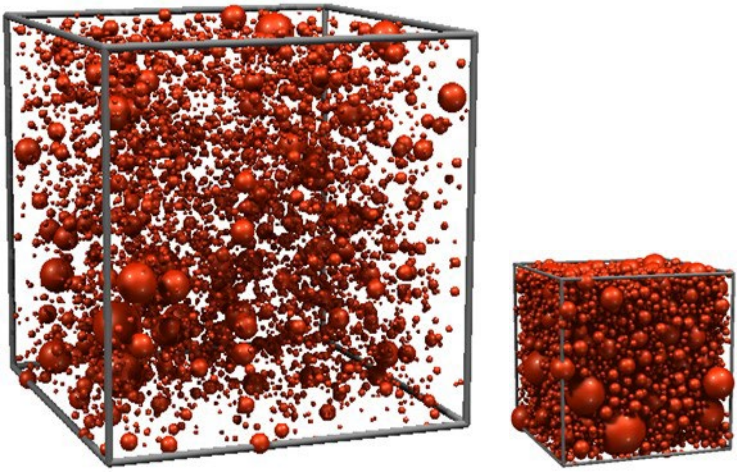

Figure 6. (left) Start of the production process by DEM of particle mixture dispersed in an enlarged container. (right) After gradual size reduction of the container the dynamic process stops at the required density (Stroeven, 1999; Le, et al., 2013).

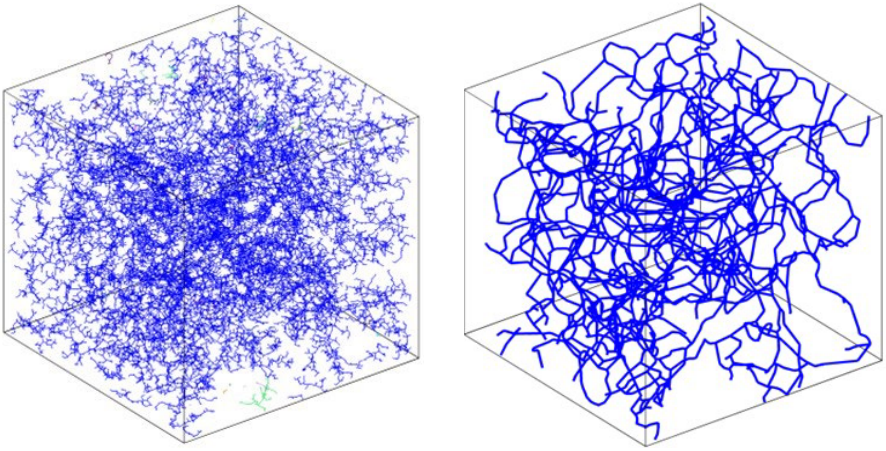

Figure 7. DRaMuTS exploration yielded the tree network structure of pores in the case of a specimen with two rigid (left and right) and four permeable surfaces. Pores meander in the 100 μm cube space through the packed system of spherical (but interfering) cement particles at 90 days of hydration (Stroeven, et al., 2012; Li, 2017). Right figure: continuous pores only.

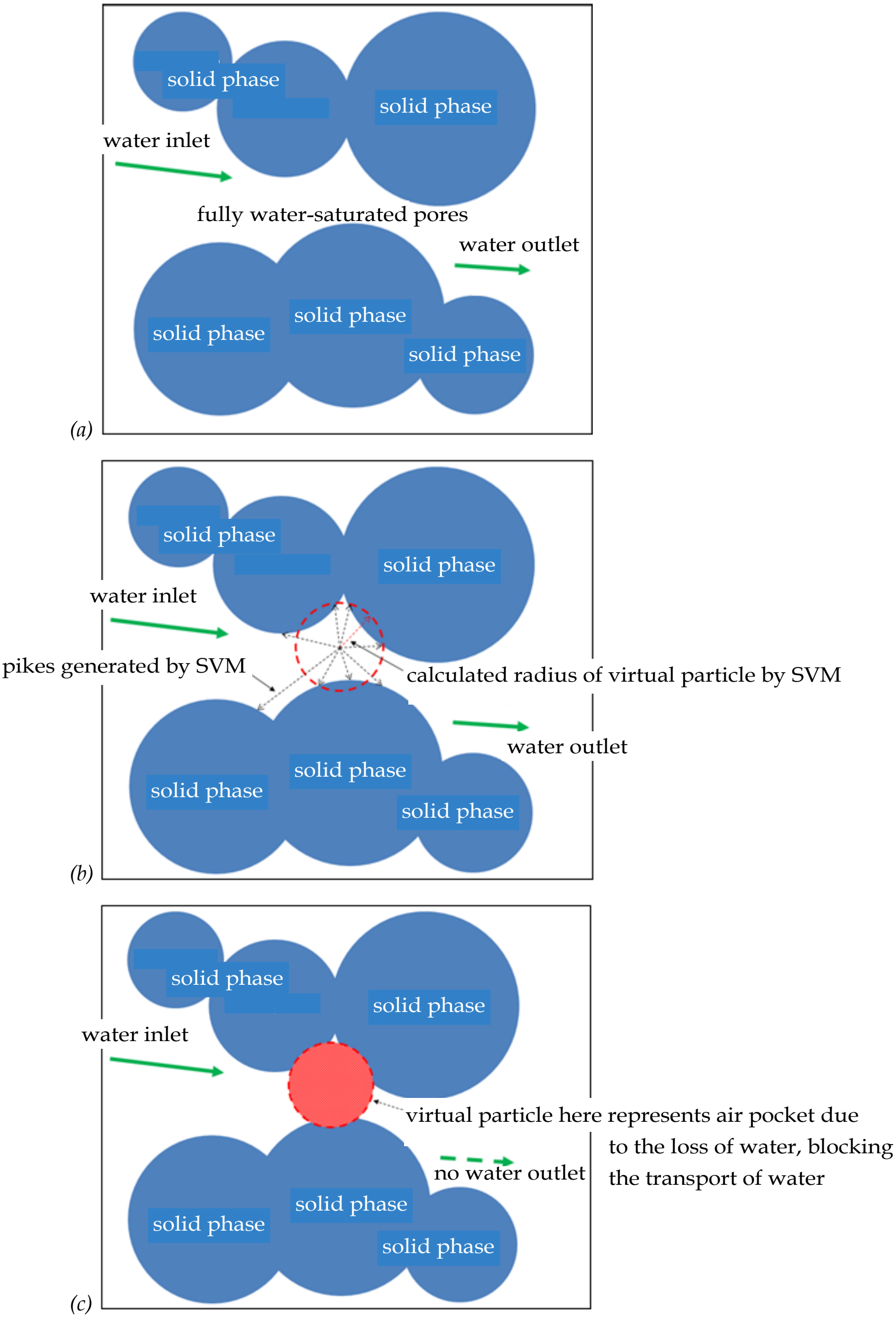

Figure 8. Blocking mechanism in virtual cement paste representing the air bubbles in the pores (Li, et al., 2016b).

5 ITZ and permeability at declining saturation degree

The pore network structure is additionally provided with size and shape information. A method adapted from life sciences is denoted star volume measuring (SVM) (Stroeven, 2019). Pore size is determined by stars in the large number of nodes shown in Figure 5. The result is a measure for the representative sphere, which has the same volume as the pore locally has. Pore length and size are combined in a pore network structure in which the pore elements are cylinders with diameters as governed by representative spheres. A reduction in conductance is accounted for by finite element approach to a couple of hundred pore sections in the virtual material. The permeability of the system is traditionally assessed by solving large numbers of linear algebraic equations, in which the unknown factors are the water transport capabilities at all nodes (Li, 2017; Li, *et al*., 2016a). The physical condition required for the analysis is *fully water-saturated cement stone*. This has been demonstrated impossible, however, even for cement stone produced under submerged conditions.

Hence, air penetrates during hardening in the pores and, in doing so, blocks water transport through the relevant pore section. As a consequence, this is the actual situation in engineering applications of concrete structures. The blocking mechanism is simulated in virtual materials as shown in Figure 8. Air more easily enters the larger pores, so that the

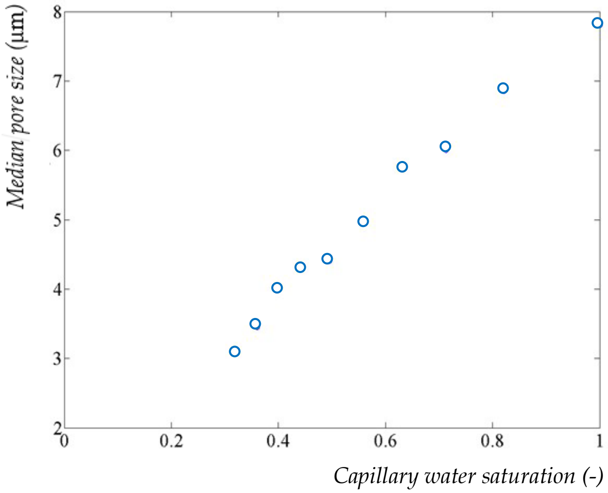

Figure 9. Almost linear reduction in median pore size with declining degree of water saturation in the capillary pore network structure

pore system that is left to transport the water is refined. This is demonstrated in Figure 9. This has consequences for permeability, of course, as confirmed by experimental data obtained on real and virtual cement paste, presented in Figure 10 (Zalzale, *et al*., (2013); Zalzale, (2014). Li, *et al*., 2016b).

6 ITZ and permeability at low-saturation degrees

So, we have seen that the permeability declines at reducing water saturation. However, bulk and ITZ zones do not show a completely similar behaviour, reflecting the differences in pore size distribution. Figure 11 demonstrates that the curves revealing the decline in water permeability, while reducing the water saturation degree, come together at low values of water saturation.

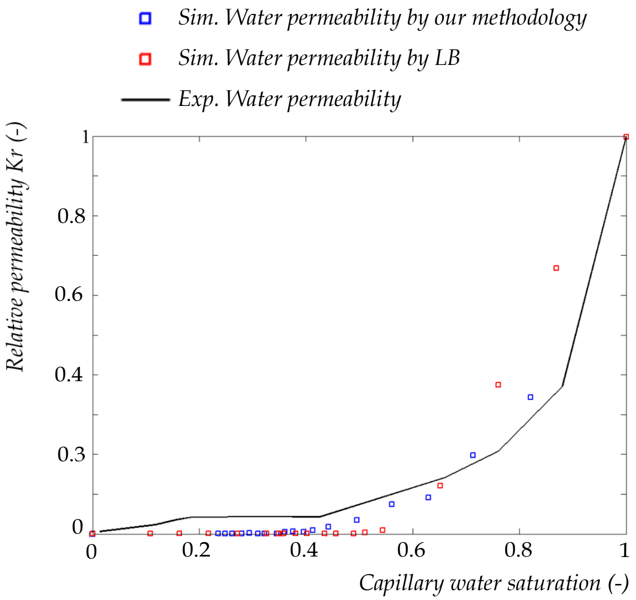

Figure 10. Effect of stagnant water content in pore system in virtual DEM-based hydrated cement paste on relative permeability K_r. Experimental data for hardened concrete with various amounts of stagnant water in the pore system is from (Kameche, et al., 2014). LB represents the Lattice Boltzmann method used for permeability calculation in RSA-based structure (Zalzale, et al., 2013). DEM data are much closer to experimental ones than those obtained by an RSA-based system.

This renders possible demonstrating in a more spectacular way what happens during hydration at different saturation degrees. Starting point is Figure 12, depicting the development of permeability during hydration in the matrix (bulk zone) and in the ITZ. Results are obtained on DEM-based virtual cement paste (Li and Stroeven, 2017). The ratio of ITZ and bulk permeabilities demonstrates the relative importance of the ITZ. The results are displayed in Figure 13, however adding the effect of partial saturation. We see

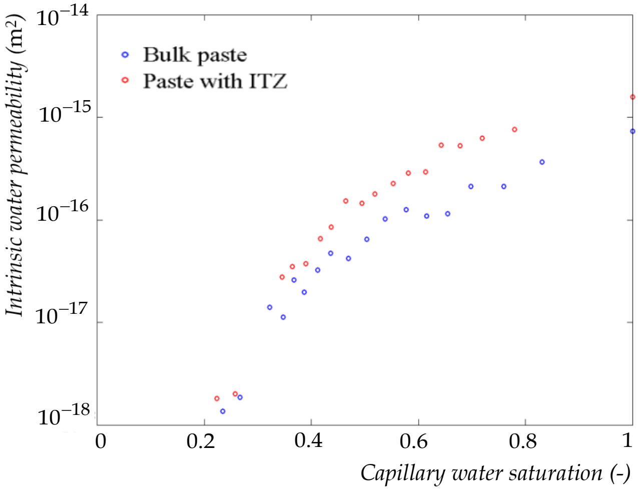

Figure 11. Influence of ITZ on water permeability of cement pastes (water/cement ratio = 0.4, hydration age: 28 days, PSD: 1 - 30 µm). Note that the intrinsic permeability is independent of the gas or fluid (in the present case water) passing through the pores as well as of the pressure gradient applied.

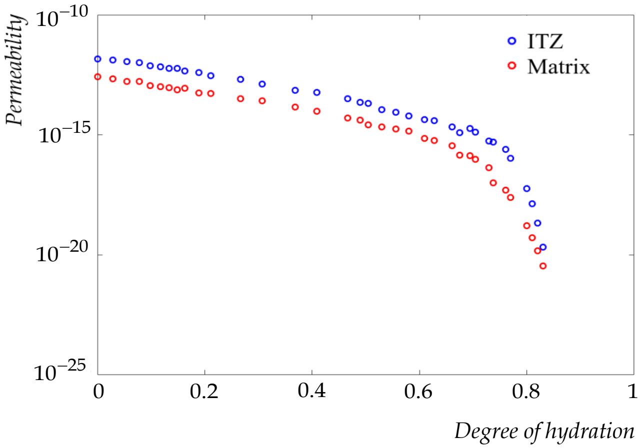

Figure 12. Permeability of the ITZ and matrix versus degree of hydration of fully saturated concrete (water/cement ratio = 0.4) (Li and Stroeven, 2017)

that near full hydration ITZ's contribution seems quite dominant. However, for relevant engineering conditions - for which it is demonstrated in earlier specified literature (*e.g.*, Zalzale, 2013; Zalzale, *et al.*, 2014) that full saturation can never be realized - this dominancy declines at reducing saturation degrees to fully disappear at 44% of partial saturation.

The final conclusion on the ITZ should therefore be: *it exists but will have only marginal impact on material properties (such as permeability) under relevant environmental conditions of concrete structures, at least in the temperate climatic zone.*

7 Evaluation and conclusion

Cement and concrete are particulate materials. Hence, understanding their structural features starts from their particulate nature. In the distribution of cement and aggregate particles alike, stochastic effects play a role. One extreme situation is only realized for very low particle contents. This state is referred to herein as "chaos". Contrary, at densest packing, order is the relevant state. So, in packed cement paste and concrete, the actual state is a mixture of both extremes. This is relevant for simulating particle packing of cement paste (and concrete aggregate). The imitation of the actual packing mechanisms is

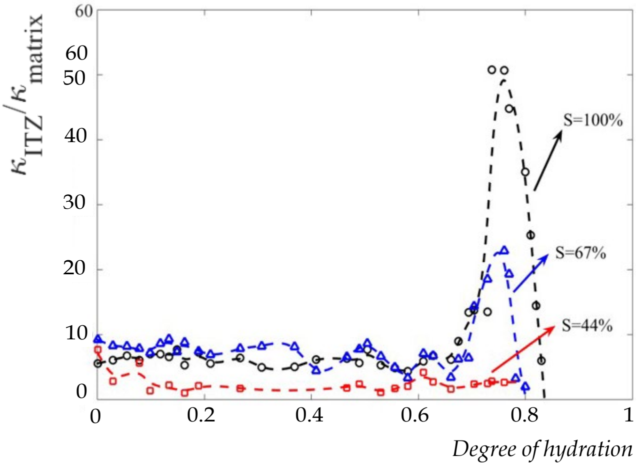

Figure 13. Permeability ratio of the ITZ to matrix versus degree of hydration of partially saturated concrete (water/cement ratio = 0.4). Dashed line is a smooth approximation of the indicated original observations (Li and Stroeven, 2017)

best guaranteed by the discrete element method-based (DEM) approaches (Li and Stroeven, 2018). All pictures in this paper are obtained on virtual material produced this way.

However, this paper stresses particularly the scientific relevance of particle packing. At close observation conditions, packing is highly irregular: the packing structure is inhomogeneous. However, heterogeneity is different for different parameters describing particulate nature. At lower magnifications, heterogeneity declines, but again different for the various parameters describing the packed system. The first parameter arriving at an "acceptable" state of homogeneity is volume fraction or weight. It is a *structure-insensitive* property. The associated homogeneous cube is referred to as the *representative volume element* (RVE) for the structure-insensitive parameter. Its linear dimension is about 5 times maximum grain size.

When the objective is to describe the *configuration* of the particles in the packed state (such as by different spacing parameters), homogeneity is obtained for a significantly larger RVE. The linear dimension of this RVE for configuration-homogeneity may exceed that for composition-homogeneity by another factor of 5 to 10. For the assessment of representative gradient structures, large domains running parallel to the interface surface have to be involved, as a consequence. This has nothing to do with the existence or not of the ITZ (Diamond and Huang, 1998). It is the logic consequence of the particulate nature that is somewhat different in the interface zone from that in bulk due to the wall effect. Moreover, gradient structures should be different for features of the particulate structure that are reflecting different configuration sensitivities, such as porosity, pore size distribution, pore spacing, degree of hydration (and resulting products).

The ITZ is more porous than bulk paste, as revealed by point density (= porosity) in Figure 5. Figure 4 presents the obtained pore characteristics, including the porosity gradient over the ITZ, The paper shows the modest differences in pore volume and size (Fig. 4) obtained by averaging over thin volume elements of maximum dimensions parallel to the interfaces. The large structural variation (inhomogeneity) on the level of individual pores prevents pores to follow the ITZ, of course (Diamond, 2003; Halamickova, *et al.*, 1995). Instead, pores meander through ITZ and bulk space, as convincingly demonstrated in Figure 7. The ITZ overlap structure (due to the packed aggregate particles) is therefore not linked up with the pore network structure, because of the same structural inhomogeneity argument. This is the reason conflicting experimental data are reported on this issue.

Porosity leads to permeability in the case of continuous pores, as depicted by Figure 7, at the right. The pore network structure in virtual hardening cement paste is readily obtained and topologically and geometrically analysed in HADES, the DEM-system on which all presented information is relying. The ITZ is demonstrated slightly more permeable, although in the fully saturated state only (Fig. 12). This has been demonstrated a hypothetical case, however. In engineering practice (as well as in research), the actual saturation degree is probably relatively low, as shown in earlier indicated studies. Since the larger pores loose water first, the active pore system refines, as demonstrated in Figure 9. The ITZ has relatively large pores, so at declining water saturation degree, the differences between bulk and ITZ permeability will disappear (Fig. 11). Figure 13, finally, presents the permeability ratio of ITZ and bulk zone for three different saturation degrees. During hydration this ratio is almost constant but reduced at declining saturation degree. Near the ultimate degree of hydration (UDH), the ratio reveals a significant peak value, i.e. five times the steady state value at lower hydration degree. The peak value can easily be understood by observing ITZ and bulk permeabilities as shown in Figure 12. Figure 13 demonstrates this peak value to drop down, and to vanish completely at a saturation degree of 0.44. See also (Shane, *et al.*, 2000). It should finally be mentioned - although far outside the scope of this article - that latest research demonstrated pores *not active in absorbing water from the environment* (such as in the splash zone of off-shore structures). This counteracts the aforementioned mechanism of open pores absorbing water.

Again, this convincingly proves that the ITZ in engineering structures of reinforced concrete is of low relevance for practical purposes as to concrete permeability.

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