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Microstructural and statistical evaluation of interfacial zone percolation in concrete

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Abstract. In freshly compacted concrete, water films form around aggregate particles, which results in a higher water/cement ratio closer to the aggregate than away from it. The interface between cement paste and aggregate, known as interfacial transition zone (ITZ), has a significantly higher porosity than bulk cement paste. This higher porosity in ITZ affects the transport properties of concrete. The Wood's metal technique was used to intrude molten metal alloy into voids and fractures in concrete which was then solidified to preserve the microstructure. The penetration of this alloy into concrete samples indicates that the porosity in the interfacial zone is permeated preferentially to the bulk paste. This technique also indicates the width of the interfacial zone in which the porosity is interconnected. The results of this experimental study were evaluated in a probabilistic sense and subject to statistical considerations. In particular, the results and interpretations of this study properly account for the aleatory and epistemic uncertainties inherent in the data.

Keywords: Cement, concrete, image analysis, scanning electron microscopy, porosity, microstructure, backscattered electron imaging, interfacial transition zone, aleatory, epistemic, uncertainties

1. Introduction

The interfacial transition zone (ITZ), which represents the interfacial region between the particles of coarse aggregate and the hydrated cement paste, is a thin shell around the aggregate and is generally weaker than either of the two components of concrete, and therefore it exercises a far greater influence on the mechanical behavior of concrete than is reflected by its size. The ITZ, the strength-limiting phase in concrete, is considered to be a zone of weakness, both in terms of strength and in terms of the permeation of fluids. The origin of the ITZ lies in the so-called "wall" effect of packing of cement grains against relatively flat aggregate surface. Aggregate particles are several orders of magnitude larger than cement grains, meaning that each aggregate particle is a mini "wall" that disrupts the packing of cement grains, resulting in a "wall" effect. This is directly responsible for the features of the ITZ, particularly in higher porosity. The differences between the properties of ITZ and those of "bulk" cement paste, or hydrated cement paste, has been studied by many researchers. It leads to a depletion of anhydrous cement in the interfacial zone, approaching zero at the aggregate surface. As a result of the anhydrous distribution there is an increase in the amount of porosity in the interfacial transition zone. Backscatter electron (BSE) images have been analyzed to measure the microstructural gradients in concrete [1–5] and it

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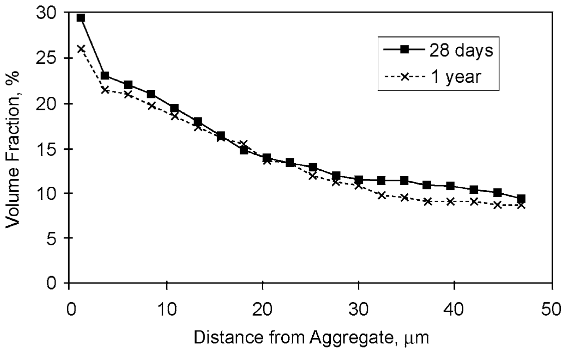

Fig. 1. Average distribution of porosity in the interfacial transition zone around aggregate particles in a concrete with w/c 0.4, from [5].

indicates that the thickness of the zone affected by the packing of the cement grains extends at least to the size of the largest cement particles, and since cement grains range in size from a micron to up to 100 microns, it may be up to 100 microns. The zone closest to the aggregate contains predominately small grains and has a significantly higher porosity, while larger grains are found further out. As packing is a random process, each individual region of ITZ will be different – the ITZ is heterogeneous on the same scale as the cement grains, therefore the average effects may not be immediately apparent in the images of concrete microstructure. There is no discrete boundary between the ITZ and the bulk paste [6]. The distance over which there is a significant increase in the porosity is only around 35–45 microns as shown in Fig. 1. The changes are progressive are most significant in the first 15–20 microns closest to the aggregate.

The effects of the interfacial zone on the permeability of concrete are not clearly established, but an earlier study indicates its important effect on transport properties of concrete [7]. Many aggregates have a lower permeability than cement paste, so their addition to cement paste might be expected to result in concrete with a lower permeability than cement paste alone, despite the introduction of the more porous interfacial zones. The effect of the anhydrous cement packing at the aggregate surfaces means that there is a higher effective water to cement ratio in the interfacial zone, which must result in a lower w/c for the bulk cement paste in concrete than for a plain cement paste having constant w/c throughout [8].

Winslow and co-workers [9–11] made a series of 28-day-old mortars with increasing sand content, but other mix parameters held constant. These mortars were examined by Mercury Intrusion Porosimetry (MIP) and it was found that above a threshold sand content of about 48% there was a disproportionate increase in the volume intruded at pressures corresponding to pore neck sizes between 0.1 and 10 microns. It was conjectured that above this critical sand content the interfacial zones became linked together or percolated. They considered that the mercury intrusion experiment is a form of "invasion percolation", in that to be intruded by mercury at below the threshold pressure, the larger pores must link up to form a continuous percolated pathway throughout the specimen. It was considered that MIP-induced percolation effect was due to the attainment of essentially complete overlap of porous interfacial transition zones thought to surround each sand grain, which requires sand content of 48% volume percentage or greater. Comparison of these experimental results with a simulation model of non-overlapping 'hard cores' representing aggregate particles with 'soft shells' representing the interfacial transition zones, Snyder et al. [10] found that an interfacial zone of 15–20 microns best explained the MIP data.

This estimate of 15–20 microns for the thickness of interfacial zones in mortars is considerably less than the distance of about 30 microns over which higher porosities were measured by Scrivener et al. [3].

The main reason for this discrepancy is that porosity will only contribute to the ingress of fluid (e.g. mercury) if it is interconnected. Simulations of cement microstructures generated by Bentz and Garboczi [12] indicate that the pore structure of cement paste becomes disconnected at volume fractions below about 18%. Referring to the curves shown in Fig. 1, in a mature paste the porosity exceeds 18% out to a distance of some 10–12 microns from the aggregate. This value is slightly lower than that estimated by Snyder et al. However, the resolution of the images used for analysis was only about 0.25 microns. This may lead to an underestimation of the total porosity of up to 3% in comparison with measurements by methanol adsorption [13].

Diamond [14] argues that the work by Winslow et al. was not based on scanning electron microscopy (SEM) investigation of the microstructure of these mortars, rather the authors relied on the conventional picture of increased pore space as a characteristic feature of the ITZ. Based on detailed backscatter SEM investigations of various mortars and concretes, he reports that hardened cement paste (hcp) in the nominal ITZ differs only slightly (on average) from hcp in the bulk of concrete with respect to the content and distribution of detectable pores. He also found that the spatial distribution of detectable pores was highly irregular, and that visibly porous patches and relatively dense patches of limited porosity intermingled irregularly in both bulk and ITZ hcps. Furthermore, many of the detectable "capillary" pores in the porous patches in both ITZ and bulk hcp were seen to be cell-like hollow shells not necessarily capable of being linked to form continuous channel [14]. He argues that the geometric overlap of ITZs at high sand contents modeled by the hard core/soft shell model does not necessarily provide continuous flow paths leading to percolation, indicating that the interpretation of their MIP findings provided by Winslow et al. in terms of percolation resulting from ITZ overlap is not necessarily correct. Diamond [14] concludes that if these higher sand content mortars are in fact percolated, the percolative effect is due to interconnected high porous hcp patches and not to geometric overlap of ITZs.

In the light of the probable importance of the interfacial zone in the penetrability of concrete, it would be very desirable to be able to examine directly the extent to which transport occurs preferentially through the interfacial zone. Furthermore, given the uncertainty present in experimental data, it is important to approach this problem statistically, looking at several specimens so that the randomness in the data can be averaged out and the interpretations and conclusions can be more accurate and general. Fortunately such an opportunity has arisen through the study in the SEM of concretes impregnated under load with Woods metal, the results of which are described in this paper.

2. Experimental technique

The equipment used for this experiment was described in detail earlier [15,16]. This experimental technique allows study the cracks in concrete samples as they exist under load. Wood's metal, whose commercial name is Cerrosafe, is a fusible alloy and in the liquid phase it is nonwetting, with an effective surface tension of about 400 mN/m. It consists of 42.5% Bi, 37.7% Pb, 11.3% Sn, and 8.5% Cd. It has a melting range from 71 to 88°C and is solid at room temperature. Wood's metal has a Young's modulus of 9.7 GPa and a density of 9.4 g/cm^3. Whilst under load the concrete is intruded with Wood's metal under a pressure of 10.3 MPa, which should penetrate pores and cracks down to 0.08 microns. After intrusion the metal is allowed to solidify before unloading. The findings presented here refer to a reference sample which was only subjected to a restraining pressure of 10.3 MPa.

A normal-strength concrete cylinder (strength $\sim$ 52 MPa), 203 mm long by 102 mm in diameter, was cast and cured at 100% RH for about 1 year. The concrete cylinder ends were ground parallel to one another with water used as the cooling fluid during cutting and grinding before testing. The concrete cylinder was then dried in an oven at a temperature of 45°C until reaching constant weight, to remove the moisture in the concrete, before placing it in the vessel for the intrusion of the molten metal. The vessel was heated to 96°C with the top cap left open. Woods metal was poured into the vessel to a level above the top end of the concrete cylinder to form a molten metal reservoir with the concrete cylinder totally submerged inside. The top cap was then immediately closed. A ceramic heater was placed around the vessel to liquefy the metal inside and to maintain a constant temperature throughout the experiment. This temperature was, in turn, monitored by a thermocouple that was attached to the side of the top cap. With the internal temperature thus established and maintained at 96°C a vacuum was applied to the vessel and kept constant for at least 30 minutes. The vacuum removed any air that had become trapped in the concrete cylinder when it was assembled into the vessel. The vacuum was then removed and a nitrogen pressure of 10.3 MPa applied to the top of the vessel, to saturate the connected pores and cracks in the sample. This condition was maintained for 2 hours to allow the liquid metal to penetrate into pores and fractures. Afterwards, fans were used to cool the vessel down to room temperature and to expedite solidification. Approximately 3 hours lapsed since the time pore pressure was applied so that the metal was allowed to solidify. After the experiment, specimens were extracted from the concrete cylinder and polished for the SEM study.

3. Discussion and statistical interpretation of the results

When analyzing experimental data one has to deal with two broad types of uncertainties: *aleatory uncertainties* (also known as inherent variability or randomness) and *epistemic uncertainties* [17]. The former uncertainties are those inherent in nature; they cannot be influenced by the observer or the manner of the observation. This kind of uncertainty is present in the size and locations of the pores in the experiment described in the previous section. The epistemic uncertainties are those that arise from our lack of knowledge, from errors in measuring observations, and from the finite size of the observation sample. This kind of uncertainty is present in the material properties and setup conditions of the experimental test. The fundamental difference between the two types of uncertainties is that, whereas aleatory uncertainties are irreducible, epistemic uncertainties are reducible, e.g., by using more accurate measurements and collection of additional samples. Below, we describe two specific types of epistemic uncertainties that arise in analyzing experimental data.

Measurement error: Uncertainty arises from errors inherent in laboratory or field measurements. The observed values could be inexact due to errors in the measurement devices or procedures. In general, the statistics of the measurement errors can be obtained through calibration of measurement devices and procedures. The mean values of these errors represent biases in the measurements, whereas their variances represent the uncertainties inherent in the measurements. This kind of uncertainty is also present when certain variables in an experiment remain unknown or cannot be directly measured. The uncertainty arising from measurement errors is epistemic in nature, since improving the measurement devices or procedures can reduce it.

Statistical uncertainty: Statistical uncertainty arises from the sparseness of data; gathering more data can reduce it. If additional data cannot be gathered, then one must properly account for the effects of this uncertainty in all predictions and in the interpretations of the results. In particular, the accuracy of one's inferences depends on the observation sample size. The smaller is the sample size, the larger is the

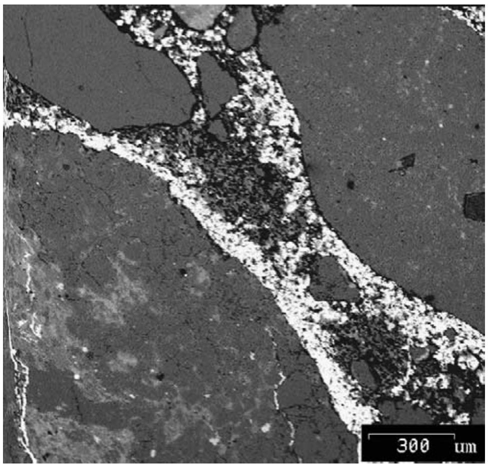

Fig. 2. BSE image of microstructure. Areas intruded with Wood's metal appear bright and are concentrated around the aggregate grains.

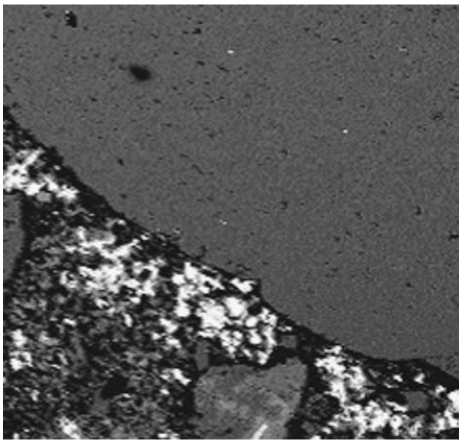

Fig. 3. ITZ around an aggregate particle at higher magnification.

uncertainty in the estimated values of the parameters. Statistical uncertainty also is epistemic in nature, as it can be reduced by further collection of data.

Given the uncertainty present in experimental data, analyses and interpretations of the results can only be done is a probabilistic sense using a statistical approach. Statistical inference gives us the tools for drawing general conclusions from experimental data, despite uncertainties. The following results are explained and illustrated for a single specimen. However, they are general and deducted from the analysis of all the experimental data.

Figure 2 is a BSE image of a concrete specimen. The bright areas are the intruded Wood's metal. It can be seen that most of the areas intruded with Wood's metal lie in the interfacial transition zones around aggregate particles, although not all these zones have been intruded. Figure 3 shows an intruded ITZ at higher magnification. There is a marked contrast between the pores in the ITZ that are filled with Wood's metal and those further from the aggregate that remain dark. The width to which the pores are filled is highly variable extending from about 30–100 microns into the paste.

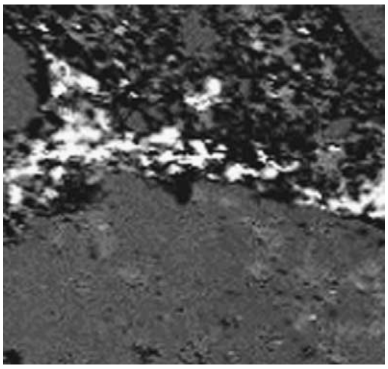

Fig. 4. BSE image of higher magnification.

The fact that groups of pores, which appear discrete on the two-dimensional sections, become filled with the intruded metal, suggests that the pores are interconnected in three dimensions and it is apparent that the tendency for pores to be connected is much greater in the vicinity of aggregate particles. It is possible that microcracks could have formed during the conditioning of the specimens or during the heating phase of the experiment. However, the temperature used during conditioning was only 45°C. Even at high magnification, Fig. 4, there is no evidence of interconnecting microcracks between the pores.

The apparent width of the ITZ in which the porosity is interconnected observed here, of 30–100 microns, appears to be considerably wider than the value of 10–20 microns discussed in the introduction. Considering just this one example, the sectioning effect cannot be corrected for and it was not possible to make enough measurements to give an average width that was statistically significant, but general observation suggested that the interconnected width was probably at least 20 microns. If the aggregate and ITZ in concrete behave as a ‘hard core/soft shell’ system, this higher width would mean that the ITZs in concrete could be percolated at quite low aggregate contents.

4. Conclusions and further work

This study gives direct evidence for the fact that the higher porosity in the ITZ results in this porosity being more interconnected and confirms that the ITZ has an important effect on the transport properties of concrete. While these observations are specific to the test conditions described in Section 2, it is believed that they are general and can be extended to other experimental or environmental conditions.

A distinction is made between the types of uncertainty one has to deal with when using experimental data. Two different types of uncertainties have been identified: aleatory uncertainty and epistemic uncertainty. This distinction has conceptual value and also important practical implications. In fact, while the aleatory uncertainty reflects the inherent randomness in the phenomena and cannot be reduced, the epistemic uncertainty can be reduced by use of more accurate measurements, of better designed experimental protocols, and the collection of more data. This distinction should guide us in deciding where to allocate our resources and in directing our efforts in a general attempt to make more accurate and reliable observations and minimize the overall epistemic uncertainty.

To further explore and validate the conclusions drawn in this research, one could prepare a set of specimens with different characteristics and conduct a similar experiment to the one conducted here. By varying one parameter at the time, one could explore the influence of w/c, curing, temperature, mix parameters, average aggregate size, effect of gravity, and other conditions that may affect the average porosity and the average width of the ITZ.

In order to be able to make sound inferences about cause-effect relationships, one would need to collect data from a properly designed set of experiments. Using a standard statistical terminology, one could use a *Completely Randomized design*, a *Randomized Block design*, a *Factorial design*, or a *Latin Square design*, to lure the sought information from the data. Statistical tests could then be used to check if the observed differences between samples are statistically significant or should be discounted as simply due to random effects.

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