Influence of the interfacial transition zone and microcracking on the diffusivity, permeability and sorptivity of cement-based materials after drying

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Abstract

Available experimental investigations on the effect of the aggregate-paste ‘interfacial transition zone’ (ITZ) on mass transport properties of cement-based materials appear to be ambiguous. Whilst some studies have found a deleterious effect of the ITZ, results from others seem to suggest otherwise. In the present study, we examined the relative influences of ITZ and microcracking on the oxygen diffusivity, oxygen permeability and water sorptivity, to further enhance our understanding of the links between microstructure and transport properties. Specimens of several neat cement pastes, mortars and concretes were prepared and tested. Variables include w/c ratio (0.3 & 0.5), binder type (CEM I & CEM II with 8% silica fume), curing period (3 and 90 days), aggregate volume fraction (0-70%) and preconditioning temperature (50°C & 105°C). 105°C drying was adapted to induce microcracking. Backscattered electron microscopy and image analysis were applied to characterise the microstructure, in particular the microcracks. We observed that in all cases, the transport properties of mortars decreased with increasing ITZ fraction. Permeability was far more sensitive to the presence of microcracking and changes in total porosity, compared with diffusivity or sorptivity. However, no critical threshold sand content linked to an ITZ percolation effect was found, even in the deliberately damaged samples. Concretes have about the same diffusivity and sorptivity, but significantly higher permeability than mortars with the same volume fraction of aggregate, despite a lower ITZ fraction. We argue that the higher permeability of concrete is due to more microcracking, and because the microcracks and paste are less tortuous than is the equivalent mortar. We also show that conventional permeability testing is affected by the sample thickness-to-maximum aggregate size ratio, which may be another factor explaining the disparity between the measured permeability of concretes and mortars.

Keywords: Interfacial transition zone; Microstructure; Microcracking; Diffusion; Permeability; Transport properties;

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1. **Introduction**

Interfaces often play a major role in controlling the properties and performance of composite materials. An important interface in cement-based composites is the ‘Interfacial Transition Zone’ (ITZ), which refers to the cement paste region surrounding each aggregate particle, where the microstructure is ‘disturbed’ by the presence of aggregates [1]. The ITZ is structurally inferior because it contains, on average, more pores and calcium hydroxide, and fewer cement particles than do the ‘bulk’ paste regions farther away [1-5]. In addition, microcracks often initiate and propagate preferentially in the ITZ, hence the common view that the ITZ is the ‘weakest link’ in concrete [6].

It is often assumed that the ITZ facilitates penetration of deleterious species into concrete. Since the ITZ is more porous, its local transport properties are expected to be higher than those of the bulk paste. In samples with high aggregate contents, adjacent ITZs would be expected to overlap and interconnect, forming a continuous porous path that spans the sample and acts as a short circuit for penetration. Indeed, computational three-phase models based on percolation theory suggest that beyond a critical aggregate content (~50% sand vol. for 20µm ITZ width), the interconnected ITZs may significantly affect bulk transport properties [7, 8]. MIP studies on mortars that found a sudden increase in intruded pore space between 45-49% sand volume fractions lend support to this prediction [9]. Interestingly, SEM studies of concretes intruded with Wood’s metal also showed that the ITZs are permeated preferentially to the bulk paste [10].

To investigate the influence of ITZ on mass/ionic transport properties, some researchers have tested model paste-aggregate composites in which neat cement paste is cast against the plane surface of a large aggregate particle [11, 12]. Whilst such studies reveal that the ITZ is indeed more penetrable than the bulk paste, they offer limited information on the overall performance of real mortars and concretes, where the microstructure is much more complicated and random. However, available studies of real mortars and concrete samples where the aggregate content is systematically increased do not provide a clear answer as to whether percolated ITZs result in higher transport properties [13-27].

On the one hand, some studies found that the bulk transport properties of mortars/concretes increase as more aggregate is added, or added past a critical amount, with the reported aggregate threshold ranging from 35-60% vol. [13-19]. Also, the often-cited observation that the permeability of a mortar or concrete is generally 10-100 times larger than that of a corresponding neat cement paste seems to lend support to the importance of ITZ percolation [13, 20]. On the other hand, some studies observed a decrease in penetrability with increase in aggregate content [21-27], suggesting that the percolation of ITZs has very little effect on global transport properties. It has also been suggested that the presence of microcracking in the ITZ is the main reason that concrete is more permeable than the corresponding cement paste or mortar [6]. Table 1 presents a summary of eleven different studies, and their main findings, to highlight this
inconsistency. It is interesting to note that these studies collectively involve a range of transport properties, sample type, maturity and moisture condition. The significance of the ITZ with regard to transport properties, it seems, remains uncertain.

The conflicting results from various sources reflect the inherent experimental difficulty in isolating the influence of the ITZ. This is partly because, when preparing and testing samples with different aggregate contents, other parameters that influence transport also vary, apart from the ITZ fraction. Sample treatment before and during testing may cause damage, particularly at the weak ITZ. For example, some transport tests require sample preconditioning to a standard moisture state, the most common method being oven drying at temperatures between 50°C and 105°C [28-30], since this is more convenient and faster than most other drying methods (e.g. drying using saturated salt solutions at room temperature). During testing, the microstructure of the sample may be altered if the test involves long exposure to water, carbon dioxide or chloride ions. Some tests are accelerated by imposing an electrical potential or by using a high pressure gradient to give measurable flow rates, which may cause additional damage to the sample. It is also well known that microcracks exist, even in samples that have not been exposed to any drying or loading. For samples with high aggregate contents, these localised microcracks could become interconnected, thereby potentially compounding any effect of the ITZ. However, most concretes in service undergo some drying, and reinforced concrete is frequently strained above its tensile capacity. Thus, concrete in real structures is almost always cracked, so testing only samples free from microcracks may be unrepresentative.

This study was undertaken to examine the relative influence of ITZ and microcracking induced by oven drying, on three different transport properties, namely gas diffusivity, gas permeability and water sorptivity. Samples with a range of aggregate content and microstructural characteristics were tested. The study also examined other experimental variables such as bleeding and sample thickness that may influence results. This work is part of a project that aims to enhance the understanding of the link between microstructure and macroproperty, in particular transport properties, in order to enable more effective modelling of the service-life and durability of concrete structures.

2. Experimental methods

2.1 Materials and mix proportions

Three series of mortars with sand volume fractions varying between 10% and up to 70% were prepared. The mixture proportions are given in Table 2. Series I and II were CEM I mortars at w/c ratios of 0.5 and 0.3, respectively, and Series III were CEM II with 8% silica fume (SF) mortars at a w/c ratio of 0.3. Equivalent neat cement paste and
concrete samples with the same w/c ratio and binder type as the mortars were also prepared. The cement oxide composition was: CaO = 65.0%; SiO₂ = 20.5%; Al₂O₃ = 5.0%; Fe₂O₃ = 2.7%; MgO = 0.9%; Na₂O = 0.19%; K₂O = 0.73%; SO₃ = 3.1% and Cl⁻ < 0.01%. The loss on ignition, Blaine specific surface and specific gravity of the cement were 1.36%, 342m²/kg and 3.15 respectively. The silica fume was an undensified type containing more than 90% SiO₂, with BET specific surface greater than 15m²/g and specific gravity of 2.2.

Thames Valley gravel (5-12.7 mm) and sand (< 5 mm) complying with the BS 882 medium grading, were used as fine and coarse aggregates, respectively. The particle size distribution and physical properties of the aggregates are given in Table 3. The low absorption values indicate that the aggregates are impervious relative to the cement paste. Since the aggregate was pre-dried, the amount of water needed to bring it to saturated, surface-dry condition was determined and added to the batch water. This was done to ensure a constant free w/c ratio across mixes from the same series, which is important because any changes in the free w/c ratio could mask or amplify the effect of ITZ on transport. This becomes significant in mixes with high aggregate contents. For example, adding dry sand with only 1% absorption can decrease the free w/c ratio of a mortar from 0.5 to 0.465, or from 0.30 to 0.275 at 60% vol. sand.

A sulphonated naphthalene-based superplasticising admixture was added to improve the workability of mixes with low w/c ratio, containing silica fume or high sand content. The batch water was also corrected for additional water brought in by the admixture. Since the mortars become less workable at increasing sand contents, mixes with high sand contents may not be compacted as well as those with low sand contents, producing another variable that may influence results. Although adding superplasticizer helps, any further increase in sand content beyond the level used in this study was not feasible.

2.2 Sample preparation

Materials were batched by mass and mixed using a pan mixer. Cylindrical samples (100Ø x 250mm) were cast and compacted in three layers using a vibrating table. The intensity and duration of the vibration was adjusted according to the workability of the mix. Each layer was compacted until no significant amount of air bubbles escaped the top surface. The compacted samples were covered with plastic sheets and wet hessian to prevent evaporation for the first 24 hours, then demoulded and sealed in cling film and polythene bags. The samples were left to cure for 3 or 90 days at 20°C. After the designated curing period, the samples were unwrapped and sectioned from the centre of each cylinder to produce three 50 mm thick discs for the mortars and concretes or three 20mm thick discs for the pastes, to be used for
transport testing. The end discs were discarded. Sectioning was done using a diamond abrasive cutter designed for brittle composite materials and was operated at slow feed rate of 0.3 mm/s.

An experimental difficulty we experienced when preparing the pastes and mortars at low sand contents, was to compact the samples without causing significant bleeding and segregation. Although care was taken to avoid over-vibration, some amount of bleeding was observed in these mixtures. This is potentially another source of error, so the water lost to bleeding was measured to ascertain if it had a significant effect on the free w/c ratio. Two parallel cylindrical samples were prepared in the same manner as before and covered to prevent evaporation. The bleed water accumulated on the top surfaces of the compacted samples was collected periodically using a pipette according to the procedure described in BS EN 480-4:2005 [31]. The measured bleed water was converted to per mass of cement from the known mix proportions, to give an estimate of the ‘corrected’ free w/c ratio.

### 2.3 Preconditioning

The discs were preconditioned to minimise the effect of moisture content on transport properties. Ideally, samples should be dried to a level where all pores relevant to transport are emptied, so that the most severe effect of the ITZ and microcracks can be measured. Our previous work [32] found that drying mature cement pastes to equilibrium at about 50% r.h., 20°C is sufficient since further drying beyond this produced only a negligible increase in transport. This seems consistent with other studies such as Parrott [29], who observed that air permeability and water absorption for concretes with a range of w/c were very sensitive to moisture content at above 60% r.h. However, drying over saturated salt solutions at 20°C would require at least six months for a 20 mm thick disc, so higher temperatures were used to reduce the conditioning time. To ensure that this was not excessively damaging, care was taken to avoid a high thermal gradient and moisture loss, particularly during the initial stages.

In the first seven days after cutting, the discs were dried at 20°C in conditioning boxes containing soda lime (to absorb CO₂) and saturated Na₂Cr₂O₇, giving a constant r.h. of about 52%. The discs were then transferred to an oven at 35°C containing silica gel. The humidity inside the oven at 35°C was generally higher than 30%. After seven days at 35°C, the temperature was gradually increased to 50°C. Saturated ZnCl₂ was placed in the oven to maintain the r.h. at 10% at 50°C; this gives the same vapour density as that at 50% r.h. at 20°C, so that a similar equilibrium moisture state is achieved. The samples were dried until equilibrium, taken as when the mass loss was no more than 0.01%/day. The entire conditioning regime typically took no more than ninety days for the 50 mm thick discs.
On the day before testing, the discs were transferred to a vacuumed desiccator containing silica gel and allowed to cool overnight to 20°C. This was done to ensure that the moisture content of the sample did not increase when its temperature was reduced from 50°C to 20°C. Checks by weighing before and after cooling in the desiccator found negligible mass change. The discs were taken out of the desiccator only when required for testing.

2.4 Transport testing

Several transport properties were examined, because the influence of ITZ and microcracking on each mechanism may not be the same. Tests were carried out on three replicate specimens following the sequence of oxygen diffusivity, oxygen permeability and water sorptivity. These were selected because oxygen transport is relevant to reinforcement corrosion, while water ingress via capillary suction is an important transport mechanism in non-saturated concrete. This sequence of testing allows the same disc to be used throughout, because successive test results are not affected by the previous tests. Therefore, three distinctly different transport coefficients can be obtained from one sample for comparison. O₂ does not react with the sample, and gaseous permeation requires a lower pressure gradient compared to liquid permeation, and is potentially less damaging. The sorptivity test completes in only several hours, thus any changes in the microstructure due to further hydration can be assumed negligible. The tests were carried out on bulk material through a cut face to eliminate possible gradient effects in the cast surface.

O₂ diffusivity was determined by exposing the opposite faces of the sample to a stream of O₂ and N₂ at equal pressure [33]. The gases counter-diffuse through the disc and the O₂ concentration in the outflow stream was measured using a zirconia analyser to calculate diffusivity. O₂ permeability was determined from the steady-state flow rate at 0.5, 1.5 and 2.5 bars above atmospheric pressure. The apparent permeability coefficient was calculated following Darcy’s equation at each pressure, from which the intrinsic permeability was determined via Klinkenberg’s correction [34]. The sorptivity test was performed using deionised water by monitoring the mass gain due to capillary absorption with time, until full saturation. The sorptivity coefficient was obtained from the slope of the regression line of absorbed water per unit inflow area against square-root of time. The coefficients of regression of the least-squares fit in the Klinkenberg method and water absorption plot were always greater than 0.99. More details of the test procedures are given in ref. [32]. On completion of the sorptivity test, the discs were immersed in deionised water and placed in a vacuum dessicator until constant mass. The sample porosity was estimated from the mass increase from the initial preconditioning state to saturated-surface dry condition.
For the ninety-day cured samples, transport tests were performed in two cycles: the first as described above and the second following oven-drying at 105°C to induce microcracking. At the end of the sorptivity test in the first cycle, the discs were immersed in deionised water and vacuum saturated. Subsequently, the saturated discs were oven dried at 105°C until constant mass, which took about 3-14 days. The discs were then cooled to 20°C in a vacuum desiccator to avoid any moisture uptake and transport tested again following the same sequence described above. Heating a saturated sample to 105°C and the ensuing removal of moisture will damage the sample in several ways. It is expected that microcracks will form preferentially at the ITZ and so samples containing high aggregate contents would be more affected. This may accentuate any negative effects of the ITZ on transport properties, in which case, it will be reflected in the difference in transport properties between the two cycles.

2.5 Influence of sample thickness

There should be a minimum sample thickness in the direction of flow so that the transport measurement can be regarded as representative. This value should be several times the maximum size aggregate (MSA) to prevent the flow being dominated by short circuits through the interface of a single aggregate particle. The typical sample thickness (t) recommended in various standard test methods is 50mm [28, 30], or three times the nominal size of the largest aggregate, i.e. t/MSA ratio ≥ 3 [30, 35]. Thinner samples can be used for testing pastes since they do not contain ITZ. However, in the studies reviewed in Table 1, various sample thicknesses have been used for testing mortars and concretes; from as thin as 3 mm [15, 18] up to 50 mm [13, 22, 23]. Where information on the aggregate size is available, we find that the t/MSA ratio ranged from about 2 [18, 25] to 20 [23].

To examine if sample thickness and the t/MSA ratio has any influence on the measured transport properties, particularly in the context of ITZ studies, we tested a three-year old mortar containing 55% vol. sand at a w/c ratio of 0.5. The mixture proportions are the same as M0.5:55 given in Table 2. Three cylindrical samples (1000 × 250mm) that had been continuously sealed cured for three years in cling film were sectioned to produce discs of thicknesses 20, 30, 40, 50 and 60 mm in three replicates, one taken from each cylinder at different heights relative to the casting direction. Considering that the maximum particle size of the sand used was 4.75 mm, this provided samples having t/MSA ratios ranging from 4 to 13. The discs were then conditioned and transport tested in two cycles following the procedures described in Sections 2.3-2.4.
2.6 Degree of hydration of pastes

The degree of hydration (DOH) was determined from non-evaporable water content by loss-on-ignition (LOI) for the paste samples. Two measurements were made in three replicates; the first was performed at the end of the 50°C preconditioning regime and the second was performed after all transport testing had concluded. Samples were crushed, placed in a crucible (approximately 50 g per test) and dried in an oven at 105°C until constant mass to remove all evaporable water. The samples were then heated to 1050°C at the rate of 5°C/min, and maintained at the peak temperature for three hours. The non-evaporable water was taken as the mass loss between 105°C and 1050°C, corrected for the LOI of the dry cement powder. The degree of hydration was then calculated as the ratio of the non-evaporable water content per gram cement to the amount at complete hydration.

2.7 Backscattered electron microscopy

A field-emission scanning electron microscope in the backscattered electron (BSE) mode was used to assess the microstructure, particularly the effect of oven drying, and to measure the volume fractions of aggregate, cement paste, air voids and microcracks via a point-counting procedure. A more detailed quantitative study of the amount and distribution of porosity, unreacted cement and hydration products will be carried out as a separate study using the Euclidean distance mapping approach [36] and reported in a future publication. Two 40×20×10 mm blocks were sectioned from the centre of each of the ninety-day cured samples, conditioned according to procedures described in 2.3 and 2.4 (i.e. dried at 50°C and 105°C), then impregnated with a low viscosity resin (pre-heated to 50°C and adding 5% toluene) and finally diamond polished in successive stages to a ¼ micron surface finish [37]. The microscope was operated at 10 keV accelerating voltage, 10 mm working distance and low vacuum (30 Pa), so sample coating was unnecessary. Fifty random locations were imaged by programming the stage to move in a grid fashion and stopping at predefined, equally-spaced coordinates. For counting the larger phases, i.e. aggregate, cement paste and air voids, a low magnification of 100× was used, giving a field of view of 1200×960μm per image at 0.5μm pixel spacing. For counting microcracks, a higher magnification of 200× was used. A 99-point grid was superimposed on the image and the phases were counted on each grid point. The total number of points counted for each sample was 4950, which should give a reasonable estimate of volume fractions. The microcrack density and specific length were also estimated from the number of intersections per unit length of the grid line, by assuming that the crack network is isotropic. This assumption is not likely to be severely violated, considering that the microcracks are caused by drying shrinkage and differences in thermal expansion between aggregate and paste, unlike load induced cracks that are more oriented and anisotropic [38].
3. Results

3.1 Bleed water measurement, point-count analysis and degree of hydration

Table 4 gives the results from bleed water measurement and point-count image analysis of selected samples that span the range of aggregate volume fraction ($V_\text{a}$) and w/c ratio studied. The pastes and mortars containing 10% vol. sand showed higher amounts of bleeding compared to other samples, particularly for the w/c 0.5 mixes. The bleeding caused a significant reduction in the free w/c ratio of P0.5 and M0.5:10 from an expected value of 0.50 to 0.45, and from 0.50 to 0.47 respectively. For samples containing higher amounts of aggregate or with a lower w/c ratio of 0.3, the effect of bleeding on the free w/c ratio appears to be small and negligible.

Results from point-count analysis show that the aggregate volume fractions agree reasonably well with expected values from mix design. This also suggests that segregation in the wet, low aggregate content mixes was probably not severe, although we note that a confirmation would require measurements taken at different heights on the cylinders. The point-count analysis also shows that mortars with high sand content (60% vol.) had significantly higher amounts of entrapped air. This indicates that they were not compacted as well as the other mixes, despite the use of superplasticizer.

The degrees of hydration for the 0.5 w/c ratio cement pastes cured for 3 and 90 days were 0.69 and 0.84 respectively. Following the completion of the transport testing, resaturation with water and drying at 105°C, the hydration degrees increased to 0.74 and 0.87 respectively. For the 0.3 w/c ratio cement pastes, the difference is lower. The degrees of hydration at the beginning (and the end) of the test sequence were 0.56 (0.60) and 0.68 (0.69) for samples cured for 3 and 90 days, respectively.

3.2 Transport properties

3.2.1 General observations

The oxygen diffusivity, oxygen permeability and water sorptivity, plotted against aggregate volume fraction for all samples from Series I, II and III are shown in Figs. 1, 2 and 3 respectively. The results are plotted in separate graphs, using a different y-axis scale for clarity. In the figures, each data point is an average of three replicates and the error bars indicate +/- one standard deviation. The variability within replicates is relatively small compared to between different samples, so averaging allows meaningful comparison to be made. However, we observed that discs extracted from the top of the cylinder tend to produce higher transport coefficients than discs from the bottom. This occurred in
most samples, even for those that showed negligible bleeding. This indicates that some segregation has inevitably occurred, which resulted in a gradient in w/c ratio and/or aggregate content along the length of the cylinders.

The collected data ranged over one order of magnitude for diffusivity and sorptivity, while permeability values covered three orders of magnitude. Unfortunately, we were unable to obtain the permeability and sorptivity values for the 105°C dried pastes because the samples failed during the second permeability test. As expected, the transport coefficients of samples with w/c 0.5 (Series I) are higher than those with w/c 0.3 (Series II & III). For samples with equal w/c and aggregate fraction, the transport coefficients decreased slightly with a longer curing age. Samples from Series III which contained silica fume recorded the lowest transport coefficients for all aggregate contents and curing ages; this is in line with well-established findings that silica fume is an effective pozzolanic micro-filler that refines the pore structure.

3.2.2 Mortar samples

Comparing the results from mortar samples only, we find that the transport properties generally showed a decreasing trend with increasing sand volume fraction. As the aggregate content increased from 10% to 70% vol., diffusivity and sorptivity decreased by a factor of 2-4 and 4-6 respectively, while permeability significantly decreased by a factor of 30-70. This suggests that the changes in cement paste volume (i.e. total porosity) and tortuosity due to increasing sand content has a more significant effect on permeability than it does on diffusivity or sorptivity. At very high sand fractions, the ITZs are ‘overlapping’ in the conventional sense if typical widths of 20-50 µm are assumed. However, there is no indication of a critical sand volume threshold, above which transport increases significantly due to percolation of interconnected ITZs. The trend remains consistent for all mortars regardless of the type of transport property, w/c ratio, binder, curing age and surprisingly even after the severe drying treatment to induce microcracking.

3.2.3 Paste samples

If the results from mortars were extrapolated, the pastes would be predicted to have higher transport properties than the mortars with dilute sand fractions. Surprisingly, this was not the case. This anomalous trend is obvious although there were exceptions in some cases. It seems to suggest that adding a small amount of inert sand can drastically increase the transport properties of the composite. Interestingly, this was also observed by Tumidajski [39] in his study of the electrical conductivities of 28-day cured mortars containing 0-35% vol. sand at w/c ratios 0.35, 0.40 and 0.45, using impedance spectroscopy. He found that in some cases, the mortar conductivities increased with increasing sand fractions from 0% to 5% vol., then subsequently decreased at higher sand fractions. This was attributed to competition between the insulating effects of the sand and the development of the ITZ. For the dilute regime, it seems that the ITZ conductivity predominates over the insulating effects of the aggregates [39].
3.2.4 Concrete samples

Results from the concrete samples show two interesting features when compared against those from mortars and pastes. Note that in Figs. 1-3, the data points for concretes are represented by a square symbol. The first striking observation is that the permeability values of concretes (highlighted in dotted circles) are significantly higher, by about 1-2 orders of magnitude, than similar mortars at equivalent aggregate content. For diffusivity and sorptivity however, the data for concretes generally obey the trend seen in the mortars, with few exceptions.

The second interesting feature is that when compared to neat cement pastes, the permeability of concretes is slightly higher, while the diffusivity and sorptivity coefficients are significantly lower than those of the pastes. If the results for the pastes are ignored, and the data from mortars at dilute sand contents are extrapolated to obtain the transport coefficients at zero aggregate content, the permeability coefficients of the concretes are about the same, if not lower, than for the hypothetical pastes. However, this would contradict the conventional notion that the permeability coefficients of mortars and concretes are typically 10-100 times larger than those of the cement pastes.

The fact that the trends observed in this study are consistent across different w/c ratios, binder types, curing ages and conditioning regimes, gives confidence that they are not caused by experimental errors or a series of coincidences. Furthermore, since the same disc sample was used for all three transport tests, in two cycles for the 90 days cured samples, and the permeability test was performed in between diffusivity and sorptivity, the trends could not be a result of sample damage during testing at any particular stage because this would be detected in subsequent tests.

It may be instructive at this point to compare the transport results of this study with others, but keeping in mind the differences in mix formulations, age, curing/conditioning regimes and test methods employed. At present, there is no other single study has examined the range of properties and samples that we have, but comparison with other disparate studies is still possible and we find that our results are in the range of reported values. For example, Carcasses et al. [23] found that the O₂ permeability of mortars (OPC: w/c 0.5 & 0.35, OPC + 10%SF: w/c 0.35) containing 10-57% vol. sand, cured for 3 days then dried at 50°C for 3 days, were in the range of \(7 \times 10^{-18} \text{m}^2\) to \(4 \times 10^{-16} \text{m}^2\). Zhu & Bartos [40] found the O₂ permeability for OPC concrete with w/c 0.57 and 0.42, and cement: sand: gravel ratio of 1: 2.1: 3.25 and 1: 1.33: 2.33 respectively, to be \(1.3 \times 10^{-16} \text{m}^2\) and \(1.0 \times 10^{-16} \text{m}^2\). The samples were water cured for seven days then dried at 55-60°C for two weeks. The sorptivity of the same samples were 248 and 181 g/m² min⁰.⁵ respectively. Shafiq & Cabrera [41] reported O₂ permeability and O₂ diffusivity values in the range of \(5 \times 10^{-17}\) to \(4 \times 10^{-16} \text{m}^2\) and \(1.4 \times 10^{-7}\) to \(2.0 \times 10^{-7} \text{m}^2/\text{s}\) respectively for OPC concretes at w/c 0.55 (1: 2.33: 3.5). The samples were cured for twenty-eight days at 65% r.h., 20°C, and then conditioned for twelve-sixteen weeks at 40% & 12% r.h. In another study, Zeiml et al. [42]
found that the air permeability of C25/30 concretes at w/c 0.49 (1:2.7:3.3) cured for twenty-eight to sixty days and dried at 105°C ranged from $1 \times 10^{-16}$ m$^2$ to $1 \times 10^{-15}$ m$^2$. Finally, Hall [43] reported sorptivity values of 120 to 250 g/m$^2$min$^{0.5}$ for OPC concretes with 0.4 w/c (1:2:4) that were oven dried at 40°C.

### 3.3 Structure of the hardened cement paste

The increase in permeability of the concretes may be attributed to ITZ effects, but this needs thorough examination. It has been suggested that the net effect of a percolated ITZ on the bulk transport property depends upon the local contrast of that particular property in the ITZ and bulk paste [8, 17, 26]. According to this theory, because permeability is a strong function of pore size and the ITZ contains pores much larger in size than those in the bulk paste, the contrast in permeability between the ITZ and bulk paste would be very high. The contrast in diffusivity, however, is lower because diffusivity is only weakly dependent on pore size. This is true, at least as far as idealised models are concerned, where it is well-known that permeability varies with pore diameter squared (all other factors being equal) [44], while diffusivity is independent of pore size for diffusion in large pores (where Knudsen effects are negligible) [45]. Therefore, ITZ plays a more important role in fluid permeability than diffusivity. This seems to be in line with our observation that the diffusion coefficients of concretes are much lower than those of the neat cement pastes and follow the decreasing trend with increasing aggregate fraction as seen in the mortars.

If a percolated ITZ is indeed the cause for the higher permeability in concretes, then one would also expect the same influence to be exerted on the mortars. Furthermore, one would expect that this influence would be seen at lower aggregate fractions because mortars contain aggregates with larger specific surface area, therefore more ITZ per unit volume so that the ITZs percolate at lower aggregate fractions than would be in the case of concretes [8, 9]. To illustrate this, Fig. 4A-C shows three composite images from BSE microscopy of 90d mortars containing 10% and 70% vol. sand, and a 90d concrete with 70% vol. aggregate from Series I (w/c 0.5). Each composite image is made up by aligning 3×3 images captured at 100× to obtain a ‘representative’ view. The images have been segmented to highlight the location of the epoxy-filled voids, i.e. capillary pores, air voids and microcracks [46], cement paste and aggregates. The samples were preconditioned in a similar way to those for transport testing (Section 2.3 & 2.4) and were oven dried at 105°C to induce the microcracks seen in the images.

By visual comparison, one can quite easily tell that the concrete contains wider cement paste (Fig. 4C) compared to the mortar (Fig. 4B), at equal aggregate volume fraction. The specific surface area of aggregates in the concrete estimated from sieve data is about 3.8 mm$^2$/mm$^3$, which is only a third of that in mortar at the same aggregate fraction (70%). The
fraction of cement paste that lies within a certain distance from the nearest aggregate surface can be measured from the images using Euclidean Distance Mapping [36] and the results are shown in Fig. 4D. For comparison purposes, data from computer simulation by Winslow et al. [9] for a mortar with 55.2% vol. sand and a concrete with 64.6% vol. aggregate, are included. Note that the aggregate size distribution used in the simulation [9] is quite similar to ours for the case of mortar, but slightly coarser for the concrete sample. If we take the conventional view that the ITZ is within 20-50μm from any aggregate surface, then our results show that a large fraction, about 65-95% of the cement paste matrix lies within the ITZ for the mortar at 70% sand vol., compared to only about 30-60% for the concrete at the same aggregate fraction. Since distances measured on a 2D section tend to overestimate the true distance, the correct curve should be slightly steeper and shifted to the left, so our estimates for ITZ fraction are actually conservative (i.e. lower than actual value). This simple comparison shows that the ITZ should have a larger influence on the transport properties of mortars than it does on concretes, but our transport results show quite the opposite. At the same aggregate fraction, mortars have about the same diffusivity and sorptivity and significantly lower permeability than that of the concretes.

3.4 Sample porosity from vacuum saturation

Fig. 5A shows the bulk sample porosities for pastes, mortars and concretes measured by water absorption under vacuum. The mass increase from the initial preconditioned state to a saturated-surface dry condition was taken as a simple estimate of the volume of pores accessible to transport. As expected, the sample porosity decreases with decrease in w/c ratio, longer curing and addition of aggregates. Samples from Series III (w/c 0.3, 8% SF) had the lowest porosities for all ages and aggregate contents. Drying at 105°C prior to vacuum saturation increases the measured porosity due to further lost of evaporable water between 50°C and 105°C, and presence of microcracks.

Fig. 5B shows the results normalised to the paste porosities. These are compared against 1-V_o representing the ideal case of a porous matrix diluted by non-porous inclusions. It can be seen that the data rarely breached the 1-V_o line. This shows that addition of aggregates and the formation of more porous ITZs do not increase the overall paste matrix porosity, which is expected since the w/c ratio is conserved. Surprisingly, the data for samples treated at 105°C also suggest that the degree of microcracking is not significantly influenced by the proportion of ITZs. In other words, drying at 105°C produced more or less the same amount of microcracks per unit volume paste, regardless of the amount of ITZ present. However, this method for measuring porosity is probably not sensitive enough to detect small changes due to microcracking.
The normalised porosities for the denser samples from Series II (w/c 0.3) and III (w/c 0.3, 8% SF) conditioned at 50\(^\circ\)C tend to fall significantly below 1-\(V_a\). This could be interpreted as a decrease in the paste matrix porosity due to addition of aggregates, but we suspect that the result is an experimental error. These samples, which have a much denser microstructure than those from Series I (w/c 0.5), were not able to fully saturate during the absorption test, and their porosities were underestimated as a consequence. However, when the same samples were dried at 105\(^\circ\)C and retested, the agreement with 1-\(V_a\) improved substantially because the induced microcracks allowed the samples to achieve a better saturation in the second absorption test.

3.5 Microcracking

Fig. 6 shows a BSE image captured at low magnification that highlights the typical microcracks seen in mortar and concrete samples that were oven dried at 105\(^\circ\)C. The microcracks have widths of about 0.5 -10\(\mu\)m and significant lengths that extend beyond the image field of view, and appear to be highly interconnected on a two-dimensional plane. Finer cracks can be seen at higher magnifications, however, these tend to be short and isolated. Samples that were dried at 50\(^\circ\)C also showed some microcracking, although not as extensive. This shows that drying even at moderate temperatures damages the microstructure. However, it should also be recognised that some of the microcracks are inherent and existed prior to the treatment imposed in this study [47, 66].

The microcracks can be divided into bond cracks that appear at the interface between aggregates and cement paste, and matrix cracks, which propagate from the aggregate surface across the cement paste in an almost linear fashion until reaching a neighbouring aggregate particle. The microcrack is either arrested here or travels around the aggregate, but sometimes it breaks and traverses through the aggregate particle, although this is rare. Therefore, the cracks tend to follow the shortest route in the paste or the boundary between the aggregate and paste, consistent with predictions from fracture mechanics. When the microstructure is examined at a lower magnification and all the images are collectively compared, the microcracks appear to be distributed over the entire sample with no preferred orientation.

The microcracks in samples with different aggregate fractions have about the same morphology and size range. There is one remarkable difference however, that in samples containing less aggregate, the microcracks are able to span wider distances before being intercepted by an inclusion (cf. Fig. 4A). In samples containing more aggregate, the microcracks have more tortuous paths and therefore larger effective lengths because they are more frequently blocked or are forced to circumvent the aggregates. Obviously, this effect depends not only on the aggregate fraction, but also on the particle size distribution. Since aggregates in concretes have a larger size distribution and therefore fewer obstructing particles...
per unit volume, it would be expected that the microcracks in the concrete samples are less tortuous compared to those in mortars at equal aggregate fraction.

Table 5 presents the estimated volume fraction, density and specific length of the microcracks using image analysis. The crack density was determined from the number of intersections per length of the grid line, \( N_L \) (mm\(^{-1}\)), while the specific length (mm/mm\(^2\)) was estimated from the well-known stereological relation of \( L_d = \frac{1}{2} \pi N_L \) [48]. The results are normalised to the paste and crack volume fractions. The data show that the neat paste samples contained significantly less microcracks than the mortars and concretes. Drying at 105°C increases the microcrack volume fraction and density, as expected. For mortars, the specific length increases with sand fraction, which supports the idea that aggregates increase the crack tortuosity, but the presence of more ITZs did not seem to produce more microcracking as we initially anticipated. The results also show that the concrete samples have more microcracks, but lower specific lengths than the mortar samples at equal aggregate volume, regardless of the w/c ratio and drying temperature.

It should be emphasised that the image analysis results are for comparative purpose only. More samples need to be examined, but the data do suggest that given the same treatment, the concrete samples cracked more than the mortars and neat pastes. The data also suggest that the effective length of the microcracks, which relates to tortuosity, is influenced by the volume fraction and size distribution of the aggregate particles. The observed microcracks are not likely to be artefacts caused by grinding or polishing during sample preparation, or by vacuum drying during SEM imaging. This is because unlike secondary electron imaging, pores and microcracks are detected in a BSE image only if they are epoxy-filled; otherwise there would be insufficient atomic contrast between them and the solid phases [37]. Since the samples are epoxy impregnated first, then ground and polished, any new cracks that formed should not be visible in the BSE images. Thus, the detectable microcracks must be due to the drying that occurred prior to epoxy impregnation, which are filled and preserved by the epoxy. Sample cutting can also produce cracks, but these are expected to be much wider than 10\(\mu\)m and confined to sample edges [49], which were not imaged.

Microcracking has the greatest effect on permeability, which increased by a factor of up to 30 when comparing the same sample dried at 50°C and 105°C. Its influence on the 0.5 w/c ratio samples (Series I) is less severe compared to the 0.3 w/c ratio samples (Series II & III). This is consistent with the expectation that the net effect of microcracks on the permeability of a more porous matrix is lower than it would be on a denser matrix. However, the diffusivity and sorptivity increased by only 10-100% when comparing the same sample dried at 60°C and 105°C. This shows that pressure-induced flow is far more sensitive to microcracking, because permeability is size dependent, while diffusion and capillary absorption are more dependent on the total porosity, which is not significantly increased by the
microcracks. There is little research that compares the effects of microcracking on permeability, diffusivity and sorptivity, but the above observation is in line with available experimental and theoretical results [32, 50].

If the crack network induced by drying shrinkage is assumed to be isotropic, we can perhaps model the cracked concrete as a simplified composite consisting of two sets of orthogonal fractures in a homogeneous matrix. Assuming that each fracture is of infinite length and has constant aperture $h$ and spacing $S$, and that the matrix is relatively impermeable such that flow under pressure occurs mainly via the fractures, the permeability of such a conceptual model can be shown to be proportional to the cube of the aperture and inversely proportional to the spacing of the fractures, i.e. equal to $h^3/6S$ [51]. Since the permeability of the 105°C dried concrete samples is in the order of $1 \times 10^{-15}$ m$^2$ (Figs. 1-3) and the crack spacing estimated from the BSE images (such as Fig. 6) is about 500μm, the effective crack aperture according to the conceptual model above would be about 1.5μm. This is in the lower range of the crack widths seen in the concrete samples. Although simplistic, the purpose of this comparison is to demonstrate that pressure-induced flow in concretes can occur preferentially and mainly via the microcracks.

3.6 Effect of sample thickness-to-maximum size aggregate ratio ($t$/MSA)

Fig. 7 shows the influence of varying the sample thickness on the measured transport properties and bulk porosity. Note that the results are normalised to the average values shown in Table 6 so that they appear on the same scale, and are plotted against sample thickness-to-maximum size aggregate ratio ($t$/MSA), which is the parameter of interest here. The sample is an OPC mortar at 0.5 w/c ratio containing 55% vol. sand that has been sealed cured continuously for three years. Each value in Table 6 is an average of fifteen measurements, taken from discs of various thicknesses (Section 2.5).

The results show that the transport coefficients and porosity of the three-year cured mortar have all decreased slightly, by 5-30% from the ninety-day cured values (Fig. 1 & Fig. 5A), due to further hydration. When the data are plotted against $t$/MSA ratio in Fig. 7, an interesting trend is obtained. Permeability increased by up to 80% when the $t$/MSA ratio decreased from 13 to 4, while diffusivity, sorptivity and porosity remained relatively constant. Although there is some scatter in the data, it seems that a $t$/MSA ratio of at least 10-12 is needed to obtain a representative permeability value for this sample. Unfortunately, we were unable to test samples thicker than 60 mm ($t$/MSA > 14) because of limitations in the test cell geometry.

The findings are unexpected because conventionally, it is assumed that a $t$/MSA ratio of 3 would be sufficient to provide representative results. For example, the NT Build 506 [35] recommends that the smallest cross section for
permeability testing must be three times larger than the nominal maximum aggregate particle size. RILEM TC 116 [30] recommends a 50 mm thick disc for gas permeability and water sorptivity measurements, which was selected on consideration that the thickness is about twice the typical reinforcement cover [28]. However, the maximum aggregate size is restricted to 20 mm, giving a \( t/MSA \) ratio of 2.5 in the most extreme case. We note that the typical sample thickness for permeability measurements of concretes is 50 mm [13, 22, 23, 52], although smaller samples of 20-35 mm have also been used [14, 16].

The increase in permeability at lower \( t/MSA \) ratio is most probably linked to the presence of microcracks, because in a relatively thin sample, there is greater possibility that the microcracks would interconnect and span its full thickness. Since bond cracks often occur at the aggregate-paste interface, the ‘representative thickness’ for permeability testing is expected to be a function of the largest aggregate size, as well as the degree of microcracking. The influence of \( t/MSA \) ratio is another factor that could explain, at least in part, the disparity between the measured permeability values of concretes and mortars. Since tests are performed on the same sample dimension, the larger aggregates in concrete effectively means a lower \( t/MSA \) ratio, which is about 4 \((=50/12.7)\) compared to 10.5 \((=50/4.75)\) for the mortars. We have seen earlier that diffusivity is less sensitive to microcracks compared to permeability, which explains why it is not affected by change in sample thickness. The sorptivity and water absorption porosity is also not expected to be influenced by sample thickness, in agreement with observations made by Dias [53].

Surprisingly, we were unable to find many studies that examined the effect of sample thickness on the measured transport properties, but available data do suggest that permeability is significantly influenced by the \( t/MSA \) ratio [54-57]. Hooton & Wakeley [54] measured the water permeability of concretes containing fly ash with maximum aggregate size of 37.5 mm using discs with thickness of 50-178 mm \((i.e. t/MSA: 1.33-4.75)\). In one set of data (0% fly ash), the permeability increased by a factor of 1.9 when \( t/MSA \) decreased from 4.75 to 3.0. In another set of data (25% fly ash), the permeability increased by a factor of 300 when \( t/MSA \) decreased from 3 to 1.33. However, when the same samples were tested at a higher confining pressure, the difference decreased to a factor of 16. This suggests that flow under pressure gradient is dominated by large microcracks, which became partially closed when a higher confining pressure was applied and/or less connected when a thicker sample was tested.

In another study, Aldea et al. [55] measured the water permeability of concretes that contained cracks of various widths induced by feedback-controlled splitting. The largest aggregate size was 4.76 mm and the test was carried out on 25 mm and 50 mm thick discs \((t/MSA \text{ ratio 5 and 10.5 respectively})\). Although the authors concluded that sample thickness had little effect on the permeability, their data did show that for an average crack opening after loading greater than about 30\( \mu \)m, the thinner samples have consistently higher permeability, by a factor of 2 to 4. The influence of \( t/MSA \) ratio on
permeability can also be deduced from tests conducted on samples containing different aggregate sizes, but keeping other parameters constant. These studies have found that increasing aggregate size, which effectively lowers the t/MSA ratio, always increases the measured permeability [56, 57]. For example, Soongswang et al. [57] observed that water permeability of concretes (w/c 0.33) containing limestone aggregates increased by 60-90% when the maximum aggregate size increased from 9.5 to 25.4 mm (t/MSA 5.3 and 2 respectively). Tests were carried out on 100 mm diameter, 50 mm thick discs.

4. Discussion

In studies such as this, it is often difficult to isolate the effects of the ITZ, because other influencing parameters inevitably vary when samples containing a wide range of aggregate contents are prepared and tested. While some of these effects can be reduced or avoided entirely, others are difficult if not impossible to control, and so must be accounted for when analysing results. One example is the amount of entrapped air voids, which is higher in mortars that contain large amounts of sand. Air voids are often assumed to play a negligible role in mass transport, since they are discrete and isolated, so they can simply be treated as inclusions that dilute the paste matrix. However, large air voids would also have their associated ITZs, and in certain cases, may be packed very close to aggregate particles (e.g. Fig. 4B). These void-paste ITZs are potentially more porous than the aggregate-paste ITZs, since aggregates can absorb some excess water in the fresh state and release it later for hydration of the surrounding paste. Also, unlike aggregate particles, air voids may not be treated as inclusions with zero conductivity depending on their degree of saturation. We do not know if these effects are significant or may cancel out, as there has been no systematic experimental study on this. However, modelling of chloride diffusivity in concrete by Bentz et al. [58] found that increasing the amount of empty air voids from 0 to 10% caused a small decrease in chloride diffusivity, suggesting that the dilution effect is more dominant.

The exact reason for the low transport properties of the neat pastes tested in this study is unknown. However, the higher bleeding in the pastes (Table 4) is clearly an influencing factor particularly at 0.5 w/c ratio. Water lost to bleeding decreases the free water content and this produced a denser microstructure in pastes compared to other samples that experienced less bleeding. Another factor is thermal expansion and drying shrinkage. The neat pastes will expand more (upon heating) and shrink more (upon drying) than the mortars and concretes, but because paste is unrestrained by aggregate, shrinkage is accompanied by less damage. Indeed, our image analysis results (Section 3.4) indicate a higher degree of microcracking in mortars compared to the neat pastes. Aggregates should not influence the cement hydration rate so it is unlikely that the neat pastes have hydrated more rapidly to produce the observed trend. In contrast, the
aggregates could release some absorbed water and promote the hydration of the surrounding ITZs, although this is trivial for dense aggregates. Related to this is the amount of excess water added to compensate for aggregate absorption. Overestimating this value will increase the free w/c ratio of the mortars, but this is also insignificant at low aggregate fractions. One notable difference in the way which the transport testing was conducted for the pastes was that thinner discs (20 mm) were used compared those for mortars and concretes (50 mm). Again, this is not expected to influence results in a way that produces the observed trend.

The influence of ITZ on bulk transport properties is not significant, despite being on average more porous and in itself more permeable. This is because the presence of more ITZs is inevitably linked to other competing effects such as reduction in the paste fraction and total porosity, i.e. the dilution effect (cf. Fig. 5), the increase in the effective transport path length, i.e. the tortuosity effect, and the presence of denser bulk matrix as a result of water conservation in the microstructure. This is in agreement with previous findings [21-27]. The higher permeability in concrete is often attributed to the porous ITZs, but our results suggest that this is more likely due to the influence of microcracks that are either inherent or induced by the drying treatment prior to testing. Since diffusivity and sorptivity are less sensitive to microcracking than permeability, these properties are not as affected.

The observed microcracks are typical of those caused by drying shrinkage as reported previously [59-62], and the widths are also in the range regarded to be important for service-life and durability [63]. In mortars and concretes, drying shrinkage is restrained by the rigid aggregates, causing a buildup of radial and tangential stresses, and finally relaxation when the local tensile strength is exceeded. Stresses are largest at the aggregate-paste interface; therefore a crack initiates here, then propagates and radiates from the aggregate surface into the paste matrix [67]. It is not surprising that the degree of microcracking in concrete is higher than an analogous mortar, when both are subjected to the same drying treatment. This is because a larger aggregate size distribution at constant volume equates to lower surface area to bond with the paste, so that any shrinkage (or expansion) produces larger stresses at the interface [63-65]. Note that the specific surface area of aggregates in the concretes we tested is only a third of that in mortars at the same aggregate volume fraction. Increasing the aggregate size at constant w/c ratio and total aggregate volume fraction is known to have a negative effect on strength and elastic properties, due to presence of more microcracks in the initial state. The work of Bisschop & van Mier [62] on drying shrinkage microcracking in cement-based composites containing spherical glass particles as aggregates illustrates this point very well. They found that given the same drying treatment, the length and depth of microcracks, measured using an optical microscope following resin impregnation, were significantly larger in samples containing bigger aggregates than those containing smaller aggregates at the same volume fraction.
It may be argued that the microstructure of the ITZ that forms in concrete is significantly different to that in mortar, thus changing the nature by which ITZ influences transport properties in mortars and concretes. For example, the larger aggregate in concrete increases the likelihood of bleed water accumulating beneath aggregates i.e. microbleeding, such that a more porous and wider ITZ is produced. Microbleeding also weakens the ITZ and increases the likelihood of microcracking. A follow-up study that examines the effect of aggregate size and volume fraction on the microstructural gradients at the ITZ using the EDM approach [36] will be carried out. However, it seems unlikely that changes in the ITZ porosity due to a larger aggregate size could be significant enough to increase the permeability by 1-2 orders of magnitude, which would be greater than the effect of increasing the w/c ratio from 0.3 to 0.5 alone. Furthermore, bleeding in samples with w/c 0.3 and containing silica fume is negligible, yet the permeabilities of these concretes are also more than 10 times greater than the equivalent mortars.

Our results showing the effect of sample thickness on measured permeability corroborates well with (limited) studies where permeability of concretes with different aggregate sizes were tested using the same disc dimension. In our case, the increase in permeability at low t/MSA ratio cannot be attributed to microbleeding, since aggregate size was constant. Nevertheless, the results should be viewed as preliminary, as more tests need to be carried out on different mixes. We do not know, for example, if the effect changes with the aggregate fraction and size distribution, w/c ratio, curing age and degree of damage. However, if the measured permeability is indeed affected when the t/MSA ratio is lower than 10-12, it would present major implications on the way we collect, interpret and use the results, for example, to validate transport and service-life prediction models. Testing the permeability of concrete samples with t/MSA ratio of 10 would present significant experimental difficulties, since this requires a sample at least 100 mm thick, thus longer preconditioning time and larger pressure gradient to provide measurable flow within reasonable steady-state time.

The drying conditions imposed in our experiments, although not significantly different from other experiments, may be relatively severe compared to natural drying of structures in-service, in which case microcracking would have been less. Further research is needed to examine the effects of microcracking due to less severe drying on the transport properties and durability of concrete. The extent of microcracking in concrete in-service and its influence on mass transport properties is also not very well understood, while this is clearly an important aspect for predicting durability and service-life.
5. Conclusions

This study was undertaken to investigate the relative importance of the aggregate-paste ITZ and drying-induced microcracking on oxygen diffusivity, oxygen permeability and water sorptivity. The main intention was to identify the phases most important to mass transport so that understanding of the link between microstructure and macroproperty, in particular durability, can be enhanced to enable more effective modelling. Samples with a range of aggregate content and microstructure characteristics were investigated. Our key findings are the following:

- The measured transport properties may be influenced by other parameters that inevitably vary when a wide range of samples are tested. These include bleeding, segregation, compaction and damage from drying, which are difficult to control and so must be accounted for when interpreting results.

- When the sand content in mortars was increased from 0% to 70% vol., oxygen permeability decreased by a factor of 30-70, while oxygen diffusivity and water sorptivity decreased by a factor of 2-4 and 4-6, respectively. The trend was consistent regardless of the w/c ratio (0.5, 0.3), binder type (with or without silica fume), curing age (3, 90 days) and even after preconditioning at 105°C to induce microcracking.

- Sample preconditioning by oven-drying induces microcracks with widths of 0.5-10μm that are interconnected and randomly orientated. Microcracking has a far greater influence on permeability than diffusivity or sorptivity. Permeability increased by up to a factor of 30, while diffusivity and sorptivity increased by only a factor of 2 at most, when comparing the same sample dried at 50°C and 105°C.

- Concrete has roughly the same diffusivity and sorptivity as its analogous mortar, but significantly higher permeability (1-2 orders of magnitude), despite having about a third less ITZ. Results from image analysis of backscattered electron micrographs suggest that the higher permeability is due to more microcracks that form in concrete compared to in the equivalent mortar, when both are subjected the same drying conditions. The microcracks and the cement paste in concrete also appear to be less tortuous compared to mortars containing equal aggregate volume fraction.

- The measured permeability is influenced by the thickness of the sample on which the test is conducted. A thinner sample exhibits a higher permeability value, probably due to microcracks that span its full thickness. Preliminary results on mortars suggest that a sample thickness of at least ten times the maximum aggregate size (t/MSA > 10) is necessary to give representative results, which may be another factor explaining the disparity between the measured permeability of concretes and mortars. This requires further investigation, but potentially has major implications on the way we measure and interpret permeability results.
• The ITZ may contain on average a higher porosity and a higher local transport property than the bulk paste, but its net effect on the overall transport property is small, even when the ITZs are overlapping. The effects of the paste volume (total porosity) and tortuosity, and presence of microcracks far outweigh any effects of the porous ITZ on transport properties, particularly permeability. Therefore, transport properties are governed by the volume fraction and microgeometry of the entire pore structure within the cement paste, not only the ITZ.

Acknowledgements

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Table 1 Summary of key experimental studies on the effect of ITZ on bulk transport properties of real mortars and concretes, arranged in chronological order. The review highlights inconsistencies in the findings obtained by different researchers.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample details</th>
<th>Transport properties</th>
<th>Main observations</th>
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<tr>
<td>Watson &amp; Oyeka, 1981 [13]</td>
<td>OPC pastes and concretes with w/c 0.3-0.8, cement content 225-625kg/m³, total aggregate content 1550-1950kg/m³ and 9.5mm max aggregate size. Samples were water cured for 27 days.</td>
<td>Oil permeability, measured on 25mm (paste) and 50mm (concretes) thick discs, after oven drying at 55°C and 105°C.</td>
<td>The permeability of concrete increased with total aggregate content (~57-74% vol.). Permeability of concretes was about 100 times greater than for cement pastes, probably due to presence of ITZ.</td>
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<td>Nyame, 1985 [14]</td>
<td>Normal and lightweight mortars at w/c 0.47 containing 20-70% vol. sand (0.6/2.4mm). Samples were water cured for 28 days.</td>
<td>Water permeability. Test conducted on 20mm thick discs.</td>
<td>Permeability increased with increasing sand content, despite the fact that total porosity decreased with addition of sand. Lightweight mortar was about twice as permeable as normal weight mortar at a given sand concentration.</td>
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<tr>
<td>Houst et al., 1993 [15]</td>
<td>OPC mortars at 0.60 w/c with cement/sand ratios 0.25, 0.43 and 0.67. Samples were cured for 28 days then carbonated prior to transport testing.</td>
<td>CO₂ and O₂ diffusivity, measured on 3-5mm thick discs, after conditioning at 55%, 76% &amp; 86% RH.</td>
<td>At low sand contents (0-50% vol.), the diffusivities decreased with sand content, but increased significantly at 55% vol. This suggests that the ITZs became percolated at higher sand contents. However, the samples may be affected by cracking due to carbonation shrinkage as a result of the pre-treatment.</td>
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<td>Halamickova et al., 1995 [17]</td>
<td>OPC mortars at w/c 0.40 and 0.50, with 0, 35, 45 &amp; 55% sand vol. Samples were cured in saturated lime solution to 45-75% degree of hydration prior to testing.</td>
<td>Chloride diffusivity and water permeability, conducted on 50mm and 35mm thick discs respectively.</td>
<td>For the same hydration degree, diffusivity and permeability of mortars were higher than cement pastes, the difference increased with increasing sand content. Permeability increased by nearly a factor of 40 between neat paste and mortar. The permeability results indicated that ITZ percolation occurred between 35 and 45% sand volume fraction for the 0.4 w/c mortars.</td>
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Hornain et al., 1995 [21]
OPC pastes and mortars at w/c 0.55, containing limestone filler and 60% vol. sand. Samples were cured for 60 days in water.

Chloride diffusivity using a simple diffusion cell, on 10mm thick discs

Buenfeld & Okundi, 1998 [22]
Concrete with cement contents of 300, 350, 400 and 450 kg/m³, at w/c 0.4 and 0.5. Maximum aggregate size was 20mm. Samples were cured for 56 days.

Chloride diffusivity decreased with addition of sand and limestone filler, indicating that the presence of ITZ has only limited effect on diffusion of chlorides.

Carcasses et al., 1998 [23]
OPC and OPC/10% SF mortars at w/c 0.50 and 0.35, containing 0.6/2.5mm river sand content varying from 10-60% vol. Samples were cured for 1 day.

Chloride diffusivity using a simple diffusion cell, on 10mm thick discs.

Buenfeld & Okundi, 1998 [22]
Concretes with cement contents of 300, 350, 400 and 450 kg/m³, at w/c 0.4 and 0.5. Maximum aggregate size was 20mm. Samples were cured for 56 days.

O₂ diffusivity, O₂ permeability, sorptivity, electrical conductivity, Cl⁻ diffusivity and carbonation resistance. Sample: 50mm thick discs.

Transport resistance steadily decreased as cement content increased for all cases, irrespective of whether the samples were pre-dried at 30°C, 50%RH or were water saturated. Increasing cement content from 300 to 450kg/m³ at constant w/c ratio equates to decreasing aggregate volume fraction from 75 to 60%.

Delagrave et al., 1997 & 1998 [24, 25]
OPC and OPC/8%SF mortars at w/c 0.25, 0.38 and 0.45, with sand content 0-57% vol. Max sand size was 3mm. Samples were cured in saturated lime for 1-3 months.

Chloride and tritiated water diffusivity, via a simple diffusion test. Sample: 5-15mm thick

Both studies found a decrease in bulk diffusivity with increasing sand content. The increased tortuosity of the paste matrix due to aggregate inclusion appeared to have a stronger influence than the interconnection of ITZ.

Shane et al., 2000 [26]
OPC mortar at w/c 0.40, silica sand content 0-50% vol.

Electrical conductivity tested at early ages of 10min up to 5 days after mixing.

ITZ did not affect the global electrical conductivity of mortar. However, significant differences in the conductivities of the ITZ and the bulk paste were observed. These were most significant when the hydration degree was between 0.5 and 0.8

Asbridge et al., 2001 [18]
OPC and OPC/10% MK mortars at w/c 0.35 and 0.40, with silica glass bead (1-1.25mm diameter) as sand at 0-55% vol. Samples were cured in NaOH for at least 60days.

Steady and non-steady state chloride diffusivity, on 3mm thick discs.

Chloride diffusivity of OPC mortar increased with sand content, a sharp rise was observed at sand vol. fraction above 35%. Diffusivity of mortars incorporating metakaolin did not vary significantly with sand vol. fraction, suggesting an improved ITZ.

Princigallo et al., 2003 [19]
Concretes with 0.37 w/c ratio, 10%SF and total aggregate of 0-75% vol. at constant coarse/ fine aggregate ratio. Max aggregate size: 16mm.

Electrical conductivity tested at early ages of 10min up to 5 days after mixing.

Results from electrical conductivity test and theoretical modelling indicated the existence of a percolating pathway through the ITZ when the aggregate exceeded 60% vol. fraction.

Table 2 Mixture proportions for paste, mortar and concrete samples prepared for this study. Notation: P = paste, M = mortar, C = concrete, SF = silica fume, SP = superplasticiser.

<table>
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<tr>
<th>Mix ID</th>
<th>Free w/c</th>
<th>Water (kg/m³)</th>
<th>Cement (kg/m³)</th>
<th>SF (kg/m³)</th>
<th>SP (% wt. cement)</th>
<th>Sand (kg/m³)</th>
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<td></td>
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<td>kg/m³</td>
<td>kg/m³</td>
</tr>
<tr>
<td><strong>Series I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>P 0.5</td>
<td>0.5</td>
<td>608</td>
<td>1216</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>M 0.5: 10</td>
<td>0.5</td>
<td>549</td>
<td>1094</td>
<td>-</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>3.</td>
<td>M 0.5: 40</td>
<td>0.5</td>
<td>372</td>
<td>729</td>
<td>-</td>
<td>-</td>
<td>1040</td>
</tr>
<tr>
<td>4.</td>
<td>M 0.5: 50</td>
<td>0.5</td>
<td>312</td>
<td>608</td>
<td>-</td>
<td>-</td>
<td>1300</td>
</tr>
<tr>
<td>5.</td>
<td>M 0.5: 55</td>
<td>0.5</td>
<td>283</td>
<td>547</td>
<td>-</td>
<td>-</td>
<td>1430</td>
</tr>
<tr>
<td>6.</td>
<td>M 0.5: 60</td>
<td>0.5</td>
<td>253</td>
<td>486</td>
<td>-</td>
<td>-</td>
<td>1560</td>
</tr>
<tr>
<td>7.</td>
<td>M 0.5: 65</td>
<td>0.5</td>
<td>221</td>
<td>425</td>
<td>-</td>
<td>0.50</td>
<td>1690</td>
</tr>
<tr>
<td>8.</td>
<td>M 0.5: 70</td>
<td>0.5</td>
<td>190</td>
<td>365</td>
<td>-</td>
<td>0.75</td>
<td>1820</td>
</tr>
<tr>
<td>9.</td>
<td>C 0.5: 70</td>
<td>0.5</td>
<td>207</td>
<td>365</td>
<td>-</td>
<td>-</td>
<td>628</td>
</tr>
<tr>
<td><strong>Series II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>P 0.3</td>
<td>0.3</td>
<td>482</td>
<td>1606</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11.</td>
<td>M 0.3: 10</td>
<td>0.3</td>
<td>435</td>
<td>1446</td>
<td>-</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>12.</td>
<td>M 0.3: 30</td>
<td>0.3</td>
<td>342</td>
<td>1124</td>
<td>-</td>
<td>-</td>
<td>780</td>
</tr>
<tr>
<td>13.</td>
<td>M 0.3: 40</td>
<td>0.3</td>
<td>292</td>
<td>964</td>
<td>-</td>
<td>0.25</td>
<td>1040</td>
</tr>
<tr>
<td>14.</td>
<td>M 0.3: 45</td>
<td>0.3</td>
<td>269</td>
<td>883</td>
<td>-</td>
<td>0.25</td>
<td>1170</td>
</tr>
<tr>
<td>15.</td>
<td>M 0.3: 50</td>
<td>0.3</td>
<td>243</td>
<td>803</td>
<td>-</td>
<td>0.50</td>
<td>1300</td>
</tr>
<tr>
<td>16.</td>
<td>M 0.3: 55</td>
<td>0.3</td>
<td>218</td>
<td>723</td>
<td>-</td>
<td>0.75</td>
<td>1430</td>
</tr>
</tbody>
</table>
### Table 3 Particle size distribution, specific gravity at ‘saturated and surface dry condition’ and absorption values of the Thames Valley sand and gravel used

<table>
<thead>
<tr>
<th>Percentage passing at sieve size (in mm)</th>
<th>Specific gravity</th>
<th>24-hr absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.7</td>
<td>99.6</td>
<td>99.6</td>
</tr>
<tr>
<td>9.53</td>
<td>76.9</td>
<td>76.9</td>
</tr>
<tr>
<td>6.3</td>
<td>99.6</td>
<td>99.6</td>
</tr>
<tr>
<td>4.75</td>
<td>71.8</td>
<td>71.8</td>
</tr>
<tr>
<td>2.36</td>
<td>55.4</td>
<td>55.4</td>
</tr>
<tr>
<td>1.18</td>
<td>41.7</td>
<td>41.7</td>
</tr>
<tr>
<td>0.6</td>
<td>22.8</td>
<td>22.8</td>
</tr>
<tr>
<td>0.425</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>0.21</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>0.15</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.075</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pan</td>
<td>2.63</td>
<td>0.9-1.3</td>
</tr>
</tbody>
</table>

### Table 4 Results from bleed water measurement and point-count image analysis of the aggregate and entrapped air void volume fractions.

<table>
<thead>
<tr>
<th>Bleeding:</th>
<th>P 0.5</th>
<th>M 0.5: 10</th>
<th>M 0.5: 40</th>
<th>M 0.5: 60</th>
<th>C 0.5</th>
<th>P 0.3</th>
<th>M 0.3: 10</th>
<th>M 0.3: 40</th>
<th>M 0.3: 60</th>
<th>C 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleed water/sample (g/kg)</td>
<td>30.4</td>
<td>17.4</td>
<td>4.32</td>
<td>3.15</td>
<td>1.06</td>
<td>8.72</td>
<td>1.57</td>
<td>0.48</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Bleed water/cement (g/g)</td>
<td>0.046</td>
<td>0.030</td>
<td>0.013</td>
<td>0.015</td>
<td>0.007</td>
<td>0.011</td>
<td>0.002</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Corrected free w/c</td>
<td>0.45</td>
<td>0.47</td>
<td>0.49</td>
<td>0.49</td>
<td>0.49</td>
<td>0.29</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

| Point-count analysis:             |       |           |           |           |       |       |           |           |           |       |
| Aggregate (% vol.)                | 0     | 9.3       | 43.2      | 58.8      | 72.9  | 0     | 10.4      | 43.4      | 57.2      | 73.2  |
| Entrapped air (% vol.)            | 2.5   | 2.5       | 3.4       | 5.7       | 3.8   | 1.7   | 1.8       | 2.9       | 7.5       | 3.4   |
| Cement paste (% vol.)             | 97.5  | 88.2      | 53.4      | 35.5      | 23.3  | 98.3  | 87.8      | 53.7      | 35.3      | 23.4  |

### Table 5 Results from image analysis (50 field per sample) of microcracks found in samples dried at 50°C and 105°C (in brackets)

<table>
<thead>
<tr>
<th>P 0.5</th>
<th>M 0.5: 10</th>
<th>M 0.5: 40</th>
<th>M 0.5: 60</th>
<th>C 0.5</th>
<th>P 0.3</th>
<th>M 0.3: 10</th>
<th>M 0.3: 40</th>
<th>M 0.3: 60</th>
<th>C 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6 Average results (15 replicates) obtained from a 3-year old, 0.5 w/c ratio mortar containing 55% sand vol.

Values shown in brackets are the coefficients of variation (%).

<table>
<thead>
<tr>
<th>Conditioning temperature</th>
<th>O₂ diffusivity (m²/s)</th>
<th>O₂ permeability (m²)</th>
<th>Sorptivity (g/m²min⁰⁵)</th>
<th>Sample porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>1.48 x 10⁻⁷ (9.0)</td>
<td>1.05 x 10⁻¹⁶ (25.9)</td>
<td>173 (7.4)</td>
<td>14.7 (3.9)</td>
</tr>
<tr>
<td>105°C</td>
<td>2.43 x 10⁻⁷ (6.6)</td>
<td>2.67 x 10⁻¹⁶ (27.0)</td>
<td>330 (8.5)</td>
<td>19.8 (3.7)</td>
</tr>
</tbody>
</table>

Figure 1 Effect of aggregate volume fraction, curing age and conditioning temperature on: A) O₂ diffusivity, B) O₂ permeability, and C) water sorptivity of samples from Series I (w/c 0.5).
Figure 2 Effect of aggregate volume fraction, curing age and conditioning temperature on: A) $O_2$ diffusivity, B) $O_2$ permeability, and C) water sorptivity of samples from Series II (w/c 0.3).

Figure 3 Effect of aggregate volume fraction, curing age and conditioning temperature on: A) $O_2$ diffusivity, B) $O_2$ permeability, and C) water sorptivity of samples from Series III (w/c 0.3, 8% SF).

(A) Mortar, 10% vol. sand

(B) Mortar, 70% vol. sand
Figure 4 Composite BSE images of 90d mortars containing sand volume fraction 10% (A) and 70% (B), and concrete at 70% aggregate volume (C) from Series I. The images have been segmented to highlight the cement paste, aggregates, pores, microcracks and air voids. The samples were preconditioned as per Sections 2.3 & 2.4 then dried at 105°C to induce microcracking. Figure (D) shows the fraction of cement paste that lies within a given distance of an aggregate surface, obtained from EDM analysis of the images and from computer modelling from Ref. [9].

Figure 5 A) Bulk sample porosity as measured from vacuum saturation, and B) normalised porosity, for all samples from Series I (w/c 0.5), II (w/c 0.3) and III (w/c 0.3 with 8% silica fume).
Figure 6 Low magnification image showing typical microcracks seen on samples that have been conditioned at 105°C. The widths of the microcracks range from 0.5-10μm. Sample is C 0.5: 90d, field of view of the BSE image is 1182 × 655μm.

Figure 7 Influence of disc thickness-to-maximum size aggregate ratio (t/MSA) on the transport properties and bulk porosity of an OPC mortar, w/c ratio 0.5 and containing 55% vol. sand that was sealed cured for 3 years. The samples were conditioned and tested in two cycles following the procedures described in Sections 2.3-2.4. The results are normalised to the average values shown in Table 6.