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Percolation due to overlapping ITZs in laboratory mortars? A microstructural evaluation

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Abstract

In a commonly cited paper [Cem. Concr. Res. 22 (1994) 25], it was found that 28-day-old mortars of sand contents in excess of ~48% by volume showed extra intruded pore space when examined by mercury intrusion porosimetry (MIP). The effect was attributed to 'percolation' of overlapping porous interfacial transition zones (ITZs), as modeled by a hard core/soft shell model. To examine the likelihood of this explanation, duplicate 28-day-old mortars were prepared with the same aggregate and cement using the same unusual mixing procedure and identical curing. The results of examination by backscatter mode SEM were not consistent with the ITZ interpretation. The hardened cement paste (hcp) in all mortars was found to consist of patches of brighter, dense, almost nonporous regions and dark, highly porous patches; the patches indifferently occupying both classical 'ITZ' and classical 'bulk' locations. Many sand grains were surrounded or partly surrounded by dense, almost nonporous hcp. The porous regions appeared to be visibly capable of supporting ready fluid transmission. In the lower sand content mortar, the porous regions were limited in extent and isolated from each other. In the higher sand content mortars, originally considered to percolate by virtue of overlapping ITZs, the proportion of porous hcp was greater and the porous hcp patches were visibly interconnected across the bulk of the mortar. Examination of recovered specimens of the original mortars, now 8 years old, showed the same microstructural features as these duplicate 28-day-old mortars. If percolation does in fact occur in the higher sand content mortars studied, it likely results from the interconnection or overlap of the coarsely porous hcp patches and not from overlap of ITZs.

Keywords: Microstructure; Backscattered electron imaging; Interfacial transition zone; Modeling; Mortar

1. Introduction

Some years ago, Winslow et al. [1] reported the results of mercury intrusion porosimetry (MIP) size distribution measurements for a series of 28-day-old mortars of increasing sand content. It was found that mortars of sand contents equaling or exceeding ~48% by volume showed increased intruded coarse pore space, i.e., space intruded at pressure less than the threshold pressure. It was 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 this MIP-induced percolation effect was due to the attainment of essentially complete overlap of porous interfacial transition zones (ITZs) thought to surround each sand grain. This was considered to require sand contents of ~48 vol.% or greater, a value in accord with the hard core/soft shell model of the ITZ published earlier by Snyder et al. [2], for the grain size distribution of the sand used in these mortars.

The paper by Winslow et al. [1] has been repeatedly cited (see, e.g., Refs. [3–5]), as direct evidence for percolation of overlapping ITZs in real mortar and concrete, and for the validity of the NIST hard core/soft shell model of the ITZ. In this model, the mortar is assumed to consist of impenetrable spherical aggregates, each surrounded by a thin concentric spherical shell that represents the ITZ. Depending on the size distribution of the aggregate and the thickness assumed for the ITZ shell, the degree of overlap of ITZs in three-dimensional space can be calculated for any volume fraction of aggregate. The result is expressed as an "ITZ fraction connected." This "ITZ fraction connected" increases with increasing aggregate content. There is a critical aggregate

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volume fraction for which the "ITZ fraction connected" is said to reach 100%, at which point the mortar or concrete is said to be completely percolated. At this point, it is considered that a continuous flow path extends through overlapping porous ITZs throughout the mass of the mortar or concrete.

It should be noted that no SEM investigation of the microstructure of these mortars was made in the original work, the authors relying 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, the present writer has questioned this conventional picture of the ITZ [6,7]. The findings of these SEM investigations indicate that hardened cement paste (hcp) in the nominal ITZ differs only slightly (on average) from hcp in the bulk of the concrete with respect to the content and distribution of detectable pores. Equally important, the spatial distribution of detectable pores was found to be highly irregular. It was found 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 channels.

These considerations suggest 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.

Thus, the interpretation of their MIP findings provided by Winslow et al. [1] in terms of percolation resulting from ITZ overlap is not necessarily correct. This is of particular concern, since these experimental results were deemed by Bentz and Garboczi [5] to "calibrate" the hard core/soft shell ITZ model, and have been extensively quoted as doing so. Indeed, it appears that the data of Ref. [1] provide almost the only cited connection between the ITZ percolation model and experimental results on real mortars or concretes.

The present work represents an attempt by the writer to help resolve the question of whether the experimental results of Winslow et al. [1] are in fact explained by overlap of ITZs. In order to do this, the details of the microstructure of mortars of the type studied by Winslow et al. were investigated by backscatter-mode SEM.

To accomplish this, 'duplicate' mortars of the three highest sand contents studied by Winslow et al. [1], specifically of sand volume percents of 44.8, 48.6 and 55.4, respectively, were prepared and hydrated for 28 days. The duplicate mortars used literally the same materials (sand and Portland cement), and the same mixing equipment and mixing and curing procedures, as were used in the original work.

In addition to examination of 28-day-old 'duplicate' mortars, some results of examination of the original mortars, stored under saturated limewater for more than 8 years, are also reported.

2. Preparation of duplicate mortars

2.1. Materials

The cement used, an ASTM Type I Portland cement produced by Lone Star Industries, was part of the stock used by Winslow et al. [1]. It had been stored in tightly sealed glass jars and not exposed to the atmosphere.

The sand used was crushed nonporous quartzite from Baraboo, WI. Residual portions of the sieved fractions of the original stock used by Winslow et al. [1] were available, and were combined by the present writer to the grain size distribution cited in that publication.

One feature not mentioned by Winslow et al. [1] was the flaky shape of many of the crushed sand grains. Many of these crushed quartzite sand particles were sharp edged and angular, as crushed hard rock particles tend to be. It would seem that modeling this particular collection of flaky, sharp sand grains as a collection of spheres represents a considerable departure from reality.

2.2. Mixing and curing procedures

In conformity with the original work, the w:c ratio used throughout was 0.40.

The details of mixing were not described in the Winslow et al. paper, but were indicated as being those previously described in an earlier publication by Winslow and Liu [8]. In point of fact, the mixing procedure used for the original mortars and duplicated here is very different from mixing methods used in conventional mortar (or concrete) mixing, in that no rotary shearing action is exerted. Instead, the mixing was done in a special evacuated chamber designed by Winslow many years ago, and used extensively at Purdue University to prepare paste or mortar mixes for MIP investigation. The object is to avoid the entrapment of air bubbles that normally takes place in conventional mixing; such air voids may distort the MIP pattern [9]. In the mixing procedure, a weighed amount of dry-blended cement and aggregate is placed in the mixing chamber, which is then evacuated. The required volume of previously de-aired water is then introduced into the chamber through a special fitting without breaking the vacuum, the water being conveyed as a thin stream impinging on the surface of the dry mass of the cement and sand mix. The chamber, still under vacuum, is transferred to the jaws of a conventional paint shaker, which is then turned on to produce a violent back-and-forth rocking motion which does the actual mixing. The mixing was done for two minutes for both the original and duplicate mortars.

After mixing, the duplicate mortars were placed in 25×80 mm plastic test tubes, in accordance with the original procedure, and consolidated by vibration using a paper vibrator. It was found that the mortars of high sand contents were harsh and difficult to consolidate; the highest sand content mortar ($\sim$55 vol.%) did not consolidate very well, and some empty gaps in the mass were subsequently detected on SEM examination.

The plastic test tubes were then sealed and allowed to stand at room temperature (23 °C) for 24 h, after which the samples were demolded and hydrated under saturated limewater for 27 additional days.

2.3. SEM specimen preparation

Specimens were prepared for backscatter SEM from each of the duplicate mortars. The actual preparation was carried out at the laboratories of the R.J. Lee Group. It involved the gentle drying, introduction of very low viscosity epoxy resin under vacuum, and then the usual grinding and polishing and carbon coating procedures to prepare a plane polished surface for examination. The specimens were cut parallel to the length of the original test tube mold rather than normal to it, so that the surface prepared for examination permitted examination from top to bottom of the cylinder. Essentially, no difference with position was found.

The SEM examinations were carried out at Purdue University using an R.J. Lee Instruments, Personal SEM.

3. Results

As indicated earlier, the present investigation was carried out to attempt to determine whether the interpretation of the MIP results reported by Winslow et al. [1] was consistent with the microstructures observed.

3.1. Examination of mortar of 44.8% sand by volume

Fig. 1 shows a representative area of the 44.8% sand mortar at low magnification.

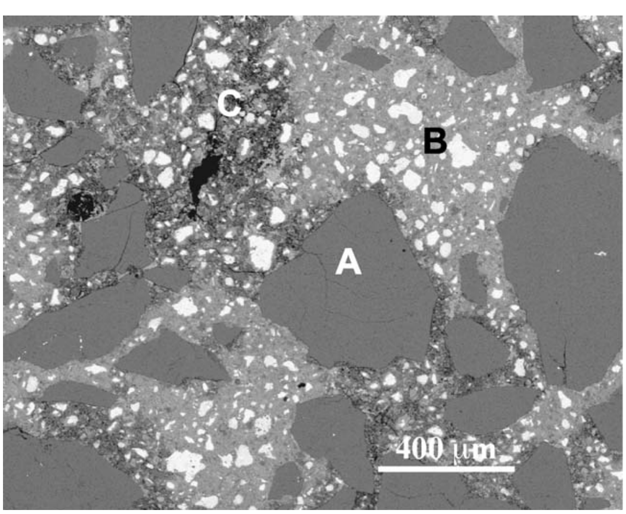

Fig. 1. Representative area of 44.8% sand mortar at low magnification. Note the uniform gray sand grains (marked "A"), the extensive areas of bright, dense hcp (marked "B") and the smaller areas of porous, darker hcp (marked "C").

More than a dozen uniformly gray sand grains of various sizes are visible in Fig. 1; a representative one is marked "A." The space between the sand grains is filled with hcp, containing various components. The very bright inclusions within the hcp are portions of residual unhydrated clinker grains. As is seen in the figure there appear to be two varieties of hcp, easily distinguished from each other. One variety is relatively bright (light gray in color) and appears to be nonporous at this low magnification. A representative area illustrating this variety of hcp is marked "B." This variety seems to be the dominant form of hcp, but it is replaced here and there by patches of a much darker and, as will be seen later, a much more visibly porous variety of hcp. A representative area of this variety of hcp is marked "C."

The largest patch of the darker, more porous hcp occupies a broad vertical band in the upper left portion of the figure, and is 400 or 500 μm in length and ca. 200 μm in width. A long, elongated empty space several hundred micrometers long occurs below and to the left of this area. Smaller areas of this darker form of hcp are ca. 100–200 μm across and occur in several distinct areas across the field.

While portions of the perimeters of some of the sand grains are in contact with the dark porous hcp patches, many portions of the perimeters of the sand grains are in direct contact with the dense, light gray hcp.

This division of the hcp into two distinct varieties is not unique in the literature. The ITZ model described by Winslow et al. [1] also considers the existence of two forms of hcp, a relatively dense 'bulk hcp' variety and a more porous "ITZ zone" variety. However, in the ITZ model, the more porous ITZ variety is thought of as surrounding the sand grains, and isolating them from the less porous bulk hcp. However, in the actual microstructure depicted in Fig. 1, the dense and porous areas are not at all distributed in the pattern assumed by the ITZ model. Rather, many sand grains are butted against dense hcp, and the largest area of the porous hcp occurs across the bulk of the mortar, away from any sand grain.

It is instructive to examine the features of the two varieties of hcp at higher magnification.

Fig. 2 shows an area of the brighter, dense hcp found in the upper right portion of Fig. 1, at a higher magnification.

As indicated previously, the bright areas in these micrographs are unhydrated portions of clinker grains; the largest one in Fig. 2 is marked "A." The entire area surrounding the residual grains has been filled in with dense hydration products. The hydration products show only a sprinkling of very small (ca. 1–2 μm) dark pores just visible at this magnification. A representative small pore, barely visible in the figure, is located immediately to the left of the location marked "B." These small pores appear to be mostly isolated from each other.

In contrast, Fig. 3, taken at the same magnification as Fig. 2, shows a typical region of the dark, porous variety of hcp.

Fig. 3 also contains the bright remnants of several unhydrated cement grains, the largest of which is marked

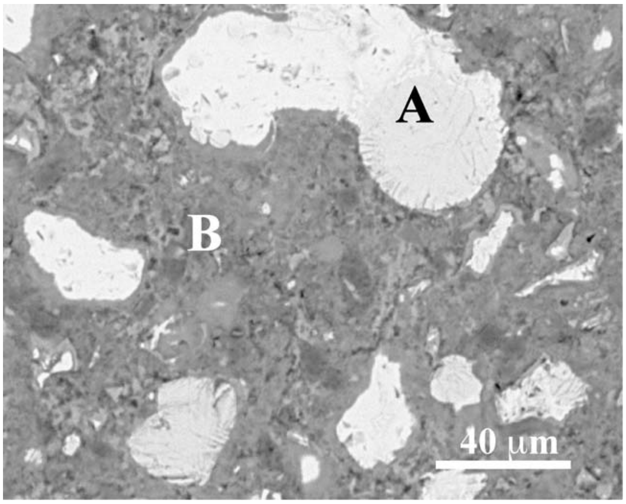

Fig. 2. Area of dense hcp at higher magnification.

"A." In contrast to Fig. 2, most of these are encased in a layer of easily visible inner C–S–H hydration product, the thickest of which is marked "B." These inner hydration products are easily separable from the surrounding porous outer product C–S–H, an area of which is marked "C." This distinction between inner and outer product is easily made here but not in Fig. 2. In the dense patches represented by Fig. 2, dense, unfilled masses of hydration product fills all of the space between the residual clinker grains. In contrast, in the porous patches depicted in Fig. 3, the areas of outer product C–S–H contain large, dark open pores up to ca. 15 μm in length. Most of these large pores appear to be interconnected. Thus, the hcp shown in Fig. 3 constitutes a highly porous zone through which ready transmission of fluids could easily take place.

In all of the present mortars, it appears that the hcp is either of the dense, light gray, almost nonporous microstructure depicted in Fig. 2 or of the porous microstructure shown in Fig. 3. Areas intermediate between the two are essentially absent.

To illustrate this point, Fig. 4, taken at the same magnification as Figs. 2 and 3, shows a boundary between dark, porous, hcp on the left and brighter, dense hcp on the right. The sharpness of the boundary is startling. Most boundary areas examined show similar sharp boundaries.

3.2. Examination of mortar of 48.6% sand by volume

This mortar, containing 48.6% sand by volume, was considered by Winslow et al. [1] and Bentz and Garboczi [5] to have a high enough sand content to provide complete percolation of the ITZs surrounding the sand grains.

Examination of this mortar at low magnification shows regions of bright, dense hcp and porous, darker hcp similar to those found the lower sand content mortar discussed previously. There is a difference in that here the proportion of the dark porous hcp patches is considerably greater, and that of bright, dense hcp correspondingly smaller, than in the previous mortar. A representative area is shown at low magnification in Fig. 5.

As seen in Fig. 5, in this mortar, the dark porous patches are not isolated from each other, and many appear to be linked in a continuous band. Such a continuous band of dark porous hcp can be traced from the left side of the lower portion of the figure horizontally to about two-thirds of the way across the figure, and then vertically almost to the top. Some connected side branches are present as well. While many of the sand grains are mostly surrounded by the dark, porous hcp; other sand grains, such as the small grains in the upper part of the figure, are mostly or entirely in contact with the dense hcp.

Fig. 6 shows an area of sand grain in direct contact with a patch of dense hcp, at higher magnification.

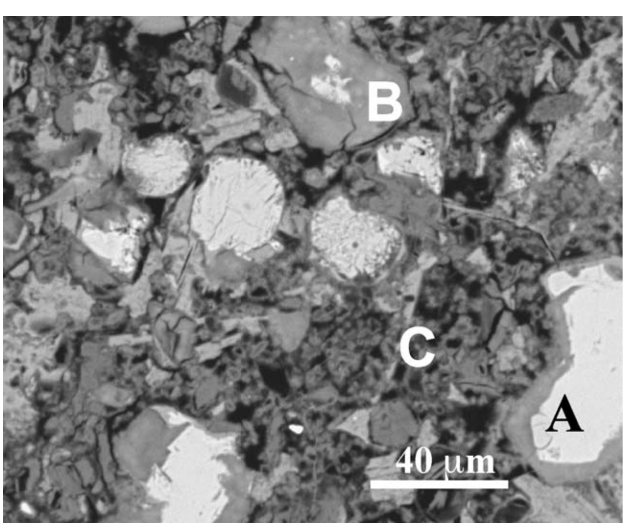

Fig. 3. Area of dark, porous hcp at higher magnification.

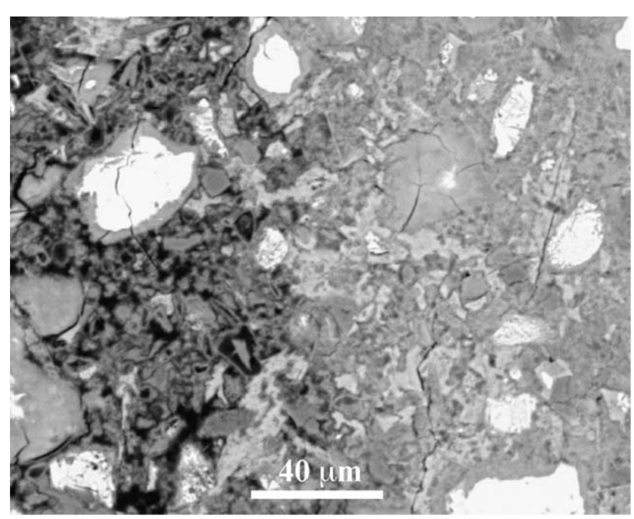

Fig. 4. Sharp boundary between porous hcp and dense hcp areas.

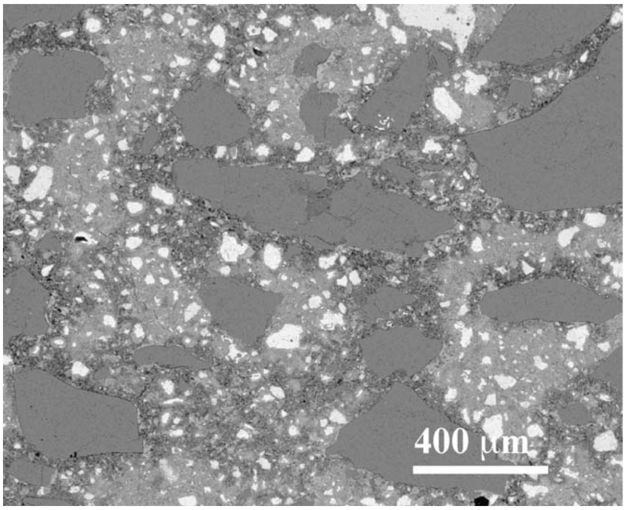

Fig. 5. Representative area of 48.6% sand mortar at low magnification.

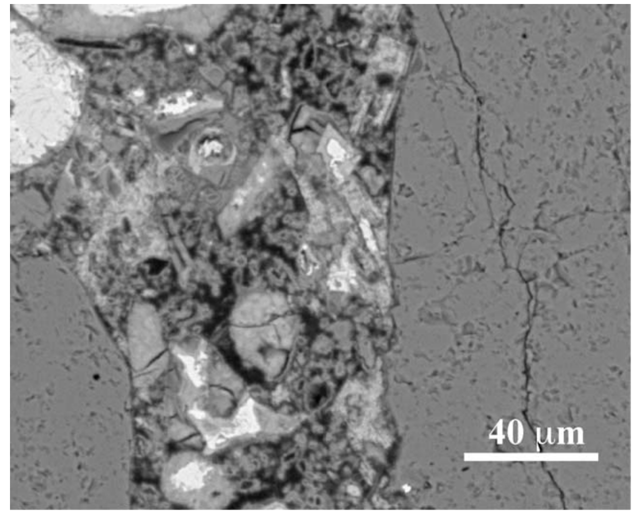

Fig. 7. Patch of dark, porous hcp between two closely spaced sand grains.

In Fig. 6, some of the area within ca. 40 μm of the sand grain surface, i.e., within the conventional ITZ zone, show a slightly higher content of visible pores than the 'bulk' hcp further away. However, these areas are very much less porous than the dark, porous hcp patches shown in Fig. 3, the left half of Fig. 4 or Fig. 7 below. Furthermore, the pores appear to be isolated rather than visibly interconnected on the plane of observation.

Fig. 7 illustrates a patch of dark porous hcp occurring between two closely spaced sand grains. Again, the characteristically large sizes of the pores and their obvious degree of interconnection even within the plane of observation are apparent. Such patches obviously would permit easy transport of fluids to a much greater degree than dense hcp, even dense hcp found close to sand grain surfaces.

Three general observations stem from close examination of various areas on this supposedly "percolating" mortar specimen. The first is that, as in the previous mortar, the patches of dense and of porous hcp are mutually distinct and the boundaries are sharp. The second is that the proportion of porous hcp is greater here than in the previous mortar, and the patches of porous hcp appear to be linked together rather than isolated. The microstructural appearance suggests that the pores within the porous hcp patches may be interconnected in three dimensions to provide a continuous pathway, i.e., to 'percolate' in the sense used by Winslow et al. [1]. The third observation is that the patches of porous hcp are in no sense identifiable as being consistent with the conventional ITZ as modeled in the hard core/soft shell model described in the various publications previously cited. The dark, porous hcp patches do not form shells around sand grains, but are spread through large portions of what conventionally would be considered bulk hcp; conversely, the porous

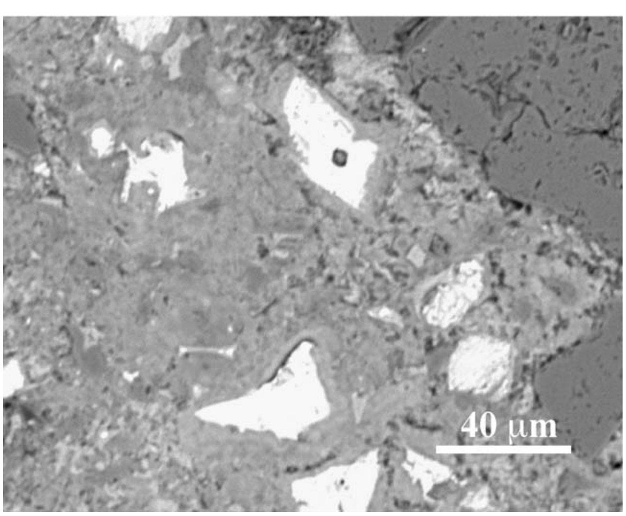

Fig. 6. Area of sand grain in contact with bright, dense hcp.

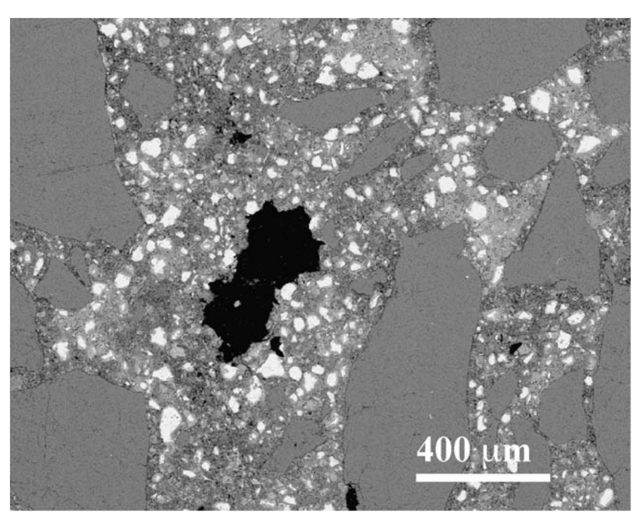

Fig. 8. Representative area of 55.4% sand mortar at low magnification.

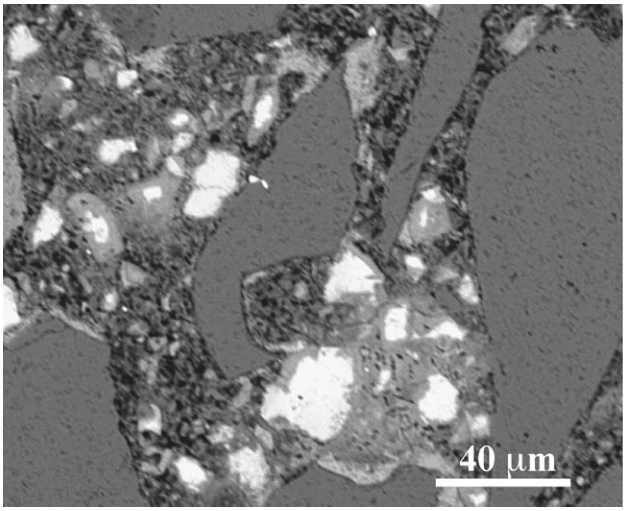

Fig. 9. An area showing mostly a porous hcp patch in 55.4% sand mortar.

hcp is absent from the immediate vicinity of many of the sand grains.

3.3. Examination of mortar of 55.4% sand by volume

According to Winslow et al. [1], this highest sand content mortar displayed an MIP curve essentially identical to that of the previous mortar, and both were considered to be fully percolated.

Fig. 8 shows a representative low-magnification view of the microstructure of this mortar. In most respects it appears similar to that of the previous mortar, with distinct patches of dense and porous hcp present. The proportions of the two types of hcp seem to be similar to those of the previous mortar, with the porous hcp again seeming to provide interconnected channels of large pores along the plane of observation.

A very large elongated void, several hundred μm long, is obvious near the middle of Fig. 8. Similar voids were found in nearly every area examined within this high-sand content mortar. They are obviously not the usual kind of air void, but rather represent spaces due to failure to completely consolidate this oversanded mortar.

A higher magnification view showing a porous hcp patch and a small area of dense hcp is shown as Fig. 9.

4. Discussion

The results of the SEM examinations above indicate clearly that the 28 day-old mortars prepared to duplicate the mortars studied by Winslow et al. [1] do not conform to the conventional ITZ model assumed in that paper. The question then arises as to whether the observations made on the duplicate mortars also reflect the microstructural characteristics of the original mortars, which were not examined by SEM prior to publication of the paper.

Fortunately, portions of these original mortars have been saved and stored under limewater since the original work was done. At the request of the writer, a brief examination of these now more than 8-year-old original mortars was recently undertaken by Amir El-Sharief at Purdue University. Fig. 10 was obtained by El-Sharief from a sample of the original 55.4 vol.% sand mortar.

It is evident from Fig. 10 that the clear division of the hcp into porous patches and dense patches found in the duplicate mortars was in fact present in the original mortars as well, and continues to be present after the prolonged additional hydration. In this micrograph, the brighter, dense hcp patch (marked “A”) occurs on the right, the darker, highly porous hcp patch (marked “B”) occurs on the left, and the boundary between the two has remained sharp.

If the pore size distribution curves cited by Winslow et al. for the two supposedly ‘percolating’ higher sand content mortars indeed represent a microstructure that ‘percolates,’ the effect is clearly due to the existence of continuous pathways through the linked patches of porous hcp, and not to overlap of ITZs as assumed in the model. Thus the statement by Bentz and Garboczy [5] (p. 362) that the model has been ‘calibrated’ against the experimental MIP data provided by Winslow et al. [1] is misleading.

The sharp division of the hcp into dense and porous regions found in these mortars was unexpected. It appears to be associated with the mixing device used in mixing these mortars, which applies a reciprocating action rather than a rotary mixing action. Nevertheless the present writer has repeatedly called attention (as for example in Refs. [6,10]) to the patchy distribution of relatively porous and relatively nonporous areas of hcp observed in conventionally mixed mortars and concretes. In mixing mortars and concretes by conventional means, the shearing of the paste under the rotary mixing and the tumbling action may to some extent act to blur the sharpness of the boundaries between dense and porous hcp patches that are observed here.

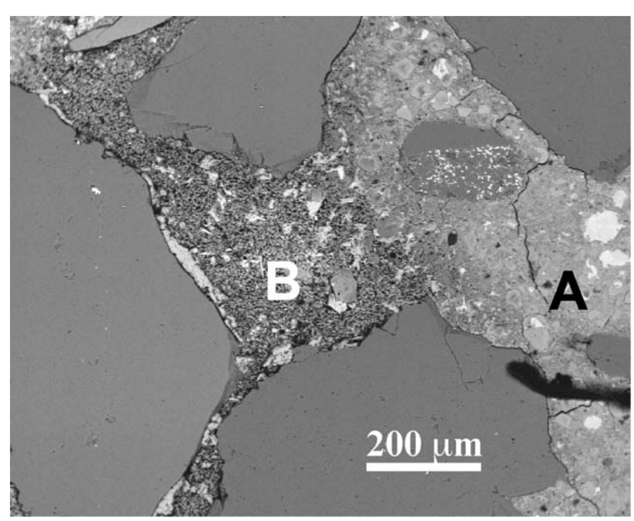

Fig. 10. Micrograph of 8-year-old original specimen of 55.5 vol.% mortar.

5. Conclusions

1. Duplicate 28-day mortars prepared to simulate those studied by Winslow et al. [1] do not show a microstructure consistent with the ITZ hard core/soft shell model assumed in that paper.
2. The microstructure actually observed consists of distinct patches of two very different forms of hcp, relatively bright, dense, only slightly porous hcp, and relatively dark and exceedingly porous hcp, the latter showing much larger and visibly interconnected pores. The two forms of hcp do not blend together, but form sharp boundaries.
3. The porous hcp is not geometrically consistent with the usual ITZ assumption, and occurs in broad patches through the bulk paste, as well as in contact with some of the sand grains; other sand grains are in contact with the dense hcp.
4. The sharp division into dense hcp and highly porous hcp was confirmed as having been present in the original mortars studied by Winslow et al. [1], by examination of portions of the original mortars which have continued to hydrate in storage for more than 8 years.
5. It appears that mortars of sand content considered by Winslow et al. [1] to be insufficient to induce percolation by overlap of ITZs show less porous hcp and the porous hcp appear to occur in patches somewhat isolated from each other. Mortars of higher sand content, considered by Winslow et al. [1] to be 'percolated' appear to have relatively high contents of the porous hcp, with the areas of this porous hcp visibly interconnected on the plane of observation.
6. If these higher sand content mortars are in fact percolated, the percolative effect is due to interconnected highly porous hcp patches and not to geometric overlap of ITZs.
7. In view of the above conclusion, the MIP experimental results cited by Winslow et al. [1] do not appear to provide experimental support for the hard core/soft shell ITZ model nor do the cited results provide 'calibration' of that model.

Acknowledgements

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