

Discussion

Reply to the discussion by Sidney Diamond of the paper “Patch microstructure in cement-based materials: Fact or artefact?”

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We thank Professor Diamond for his comments on our paper.

Concrete is a heterogeneous material, the heterogeneity occurring across several length scales. In the microstructure of cement paste, the distribution of phases: cement grains, hydration products and pores is *not* uniform. Microscopically, some areas may contain a larger local concentration of cement grains, while other areas appear to be more porous. Particle-packing effects, local variation in w/c ratio, micro-bleeding on aggregate surfaces, etc. or defects such as insufficient mixing and carbonation, are possible causes. However, these micro-scale inhomogeneities are not considered to be what is termed ‘patch microstructure,’ as presented by Diamond in Refs. [1] and [2].

Patch microstructure refers to broad areas, in the order of several hundred microns or more [1,2], of dense, almost non-porous paste, and dark, highly porous paste, that are separated by sharp and distinct boundaries [1]. These patches are irregularly shaped and occur randomly in ‘bulk’ and classical ‘ITZ’ paste. The most striking feature of patch microstructure is the *sharp boundary* between the porous and dense paste, as shown in Fig. 1A. We emphasise that the characteristics of patch microstructure given here, or in our paper [3], are identical to those originally reported in Refs. [1] and [2].

We showed that patch microstructure is an artefact of sample preparation: the appearance of dense paste in a backscattered electron (BSE) image is a false impression due to areas that have been ground beyond the epoxy resin intrusion depth. When the same sample is re-impregnated with epoxy and re-polished, we found that the sharp boundaries and dense paste disappeared, replaced by paste that showed many capillary pores and hollow-shells previously not seen (Fig. 1B). Nevertheless, there remain some areas that have a higher local concentration of large unreacted cement grains (circled in Fig. 1B), but these micro inhomogeneities are *not* the broad dense patches in the context

of ‘patch microstructure’ because: (1) no sharp boundaries exist, and (2) the size is much smaller.

We appreciate Professor Diamond providing details of the sample preparation procedure used at Purdue University. We are aware of the vinyl cyclohexene dioxide based resin, a.k.a. Spurr’s resin [4] that has lower viscosity than araldite, but we have avoided using it due to its carcinogenic effect and the need for heat treatment to harden the resin. We agree that the 5–6 mm of epoxy intrusion reported to be achieved at Purdue using this method is sufficient. However, the samples that showed the original patch microstructure reported in Refs. [1] and [2] were *not* prepared at Purdue, but at the R.J. Lee Group. According to Diamond [5], the R.J. Lee Group uses a different epoxy and a different impregnation procedure: a conventional two-part epoxy under vacuum that penetrates only around 150 μm into a 0.4 w/c ratio concrete, which is consistent with what has been reported previously [6,7]. With such limited epoxy penetration, there is a high risk that some parts of the sample may be ground beyond the impregnated depth, as we have described in Ref. [3].

In his discussion of our paper, Professor Diamond presents two BSE images that supposedly show patch microstructure in fully impregnated concrete samples of w/c ratio 0.35 and 0.5 (Figs. 1c and 3a in Ref. [5]). We feel that these do not conform to the patch microstructure originally described in Refs. [1] and [2], i.e. alternating broad dense/porous patches, but show local areas with higher concentrations of unreacted cement grains. No sharp boundaries can be seen between the allegedly porous and dense areas in either figure.

Professor Diamond also presents a secondary electron (SE) image that supposedly shows patch microstructure in a non-impregnated concrete sample (Fig. 2c in Ref. [5]). The secondary mode of the electron microscope gives topological contrast for viewing fractured surfaces, but for flat-polished non-impregnated surfaces, cavities may form bright illumination at their edges or across their entire area, due to charge accumulation. Such bright cavities could be from inherent

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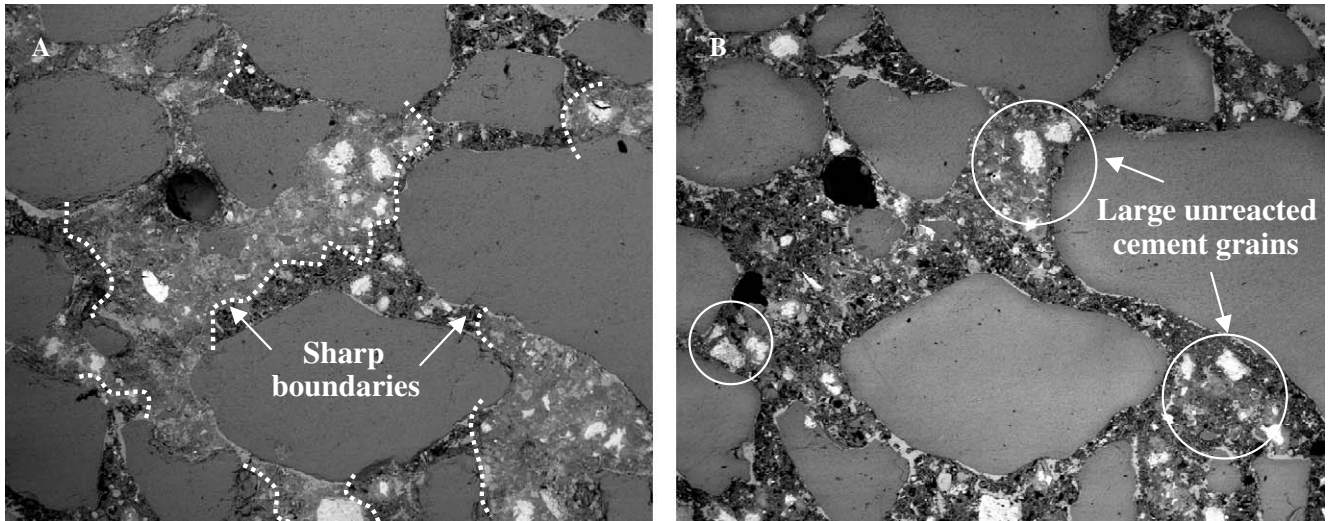


Fig. 1. (A) BSE image of 'patch microstructure' in a 28-day OPC mortar at w/c ratio 0.6 featuring sharp boundaries between the dense and porous paste; (B) BSE image of the same area showing that the sharp boundaries and dense paste have 'disappeared' after re-impregnation with epoxy and re-polishing. Some areas (circled) contain a higher local concentration of large, unreacted cement grains. These are not 'patch microstructure.' Field of view is $1333 \times 1000 \mu\text{m}$.

pores, but also from *surface defects* such as particle pull-outs, cracks and surface relief. Since non-impregnated samples are prone to damage during grinding and polishing, it is not possible to tell whether the bright features observed in SE mode are inherent pores or sample damage. Therefore, the conclusion that dense and porous patches were observed using SE mode in a non-impregnated polished surface is flawed.

In fact, the two BSE images presented by Professor Diamond (Figs. 2b and 3a in Ref. [5]) of a non-impregnated and a fully impregnated sample, illustrate our point that the presence of epoxy is crucial to provide atomic contrast for imaging pores. The BSE image of the non-impregnated sample (Fig. 2b) contains significantly less visible porosity than the fully impregnated sample (Fig. 3a). This despite the fact that both images came from similar concretes (w/c 0.5), captured at the same magnification, under the same microscope settings.

We reiterate that the appearance of patch microstructure, i.e. broad dense and porous regions separated by sharp distinct boundaries, is an artefact of sample preparation and does not reflect the true nature of the hydrated cement paste. The appearance of dense patches comes from areas that have been ground beyond the epoxy intrusion depth. In a BSE image, non-

resin filled pores are not visible because backscatter electrons are generated from the base or side walls of the pores.

References

- [1] S. Diamond, Percolation due to overlapping ITZs in laboratory mortars? A microstructural evaluation, *Cem. Concr. Res.* 33 (7) (2003) 949–955.
- [2] S. Diamond, The microstructure of cement paste and concrete — a visual primer, *Cem. Concr. Compos.* 26 (8) (2004) 919–933.
- [3] H.S. Wong, N.R. Buenfeld, Patch microstructure in cement-based materials: Fact or artefact? *Cem. Concr. Res.* 36 (2006) 990–997.
- [4] A.R. Spurr, A low-viscosity epoxy resin embedding medium for electron microscopy, *J. Ultrastruct. Res.* 26 (1–2) (1969) 31–43.
- [5] S. Diamond, A discussion of the paper "Patch microstructure in cement-based materials: Fact or artefact?" by H.S. Wong and N.R. Buenfeld, *Cem. Concr. Res.* 36 (2006) 998–1001.
- [6] K.O. Kjellsen, A. Monsøy, K. Isachsen, R.J. Detwiler, Preparation of flat-polished specimens for SEM-backscattered electron imaging and X-ray microanalysis — importance of epoxy impregnation, *Cem. Concr. Res.* 33 (2003) 611–616.
- [7] U.H. Jakobsen, P. Laugesen, N. Thaulow, Determination of water–cement ratio in hardened concrete by optical fluorescence microscopy, in: M.S. Khan (Ed.), *Water–cement Ratio and Other Durability Parameters: Techniques for Determination*, SP 191-3, ACI International, Los Angeles, 2000, pp. 27–41.