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Discussion

A discussion of paper “Patch microstructure in cement-based materials: Fact or artefact?” by H.S. Wong and N.R. Buenfeld

Sidney Diamond

School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN 47907-2051, USA

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I thank Mr. Wong and Professor Buenfeld for their courtesy in supplying a draft copy of their paper prior to publication.

These authors concluded that the patchy structure of concrete and mortar, as illustrated by the present writer in various publications, is an artifact produced by failure of the epoxy resin to uniformly occupy different areas of the surface of the specimen being examined. They assert that the dense patches seen in backscatter SEM are not actually present, but reflect backscatter from the areas on the surface that do not have epoxy present and are in fact porous.

This assertion is erroneous. The patch structure in backscatter SEM is visible in fully impregnated specimen surfaces. It is equally evident on surfaces completely lacking in epoxy. The reality of the dense and porous areas is also obvious in secondary electron mode (SEM) on unimpregnated surfaces. The patch structure is also evident in optical microscope examination of thin sections. None of these modes of examination is subject to the alleged artifact.

Wong and Buenfeld have questioned the details of the specimen preparation and impregnation procedures used by the present writer. Concrete specimens at Purdue University have been prepared for backscatter SEM examination for almost 20 years in essentially the same way. Small prisms are cut from the concrete (or mortar) to be examined and dried before epoxy penetration. Drying procedures have varied slightly, but are more rigorous than those commonly used by others since the epoxy medium we use is sensitive to moisture. Typically, drying is done in an oven for several days at temperatures of at least 50 °C; sometimes further drying at 105° has been used. This rigorous drying may conceivably induce some additional cracking, but no other effects visible at the magnifications used in backscatter SEM have been recognized.

The epoxy resin and the method of impregnation are both quite different (and much more effective in achieving penetration) than those used by Wong and Buenfeld. We use the Spurr epoxy medium [1], a four-component ultra-low viscosity system developed many years ago specifically for maximum penetration into dense structures. It is widely used in electron microscopy of biological materials. Unlike conventional two-part epoxy mixes, no appreciable polymerization takes place while the epoxy is impregnating the sample, permitting long impregnation times. The mix retains its low viscosity indefinitely at room temperature; polymerization and hardening require a separate heating step at 70 °C. In our procedure the dried specimen, typically a prism ca. 10–12 mm thick and ca. 15 to 20 mm on a side, is placed in a 30 mm diameter, 30 mm high plastic mold in the open atmosphere, and surrounded by the freshly mixed liquid epoxy. The mold and its contents are next transferred to a desiccator and evacuated continuously for at least 4 h, and sometimes overnight. De-airing of the pores in the specimen takes place through the surrounding fluid epoxy, as evidenced by the bubbling which typically takes place for about the first hour. The impregnated specimen is then removed and hardened at 70 °C. For difficult-to-penetrate low w:c concretes, instead of the ca. 100–150 μm depth of penetration found with conventional epoxies, examination almost always shows penetration of the epoxy deep into the specimen; typically penetrations of ca. 5 or 6 mm are found down from the top, up from the bottom, and in from around the periphery. We then use a slow-speed wafering saw to create the surface to be examined well within the impregnated zone; the cut is normally placed ca. 1–2 mm below the top of the specimen. The subsequent grinding and polishing procedures are straightforward; we use diamond-embedded metal plates for coarse grinding, and diamond paste spread on polishing cloths for final polishing to ¼ μm.

E-mail address: diamond@ecn.purdue.edu.

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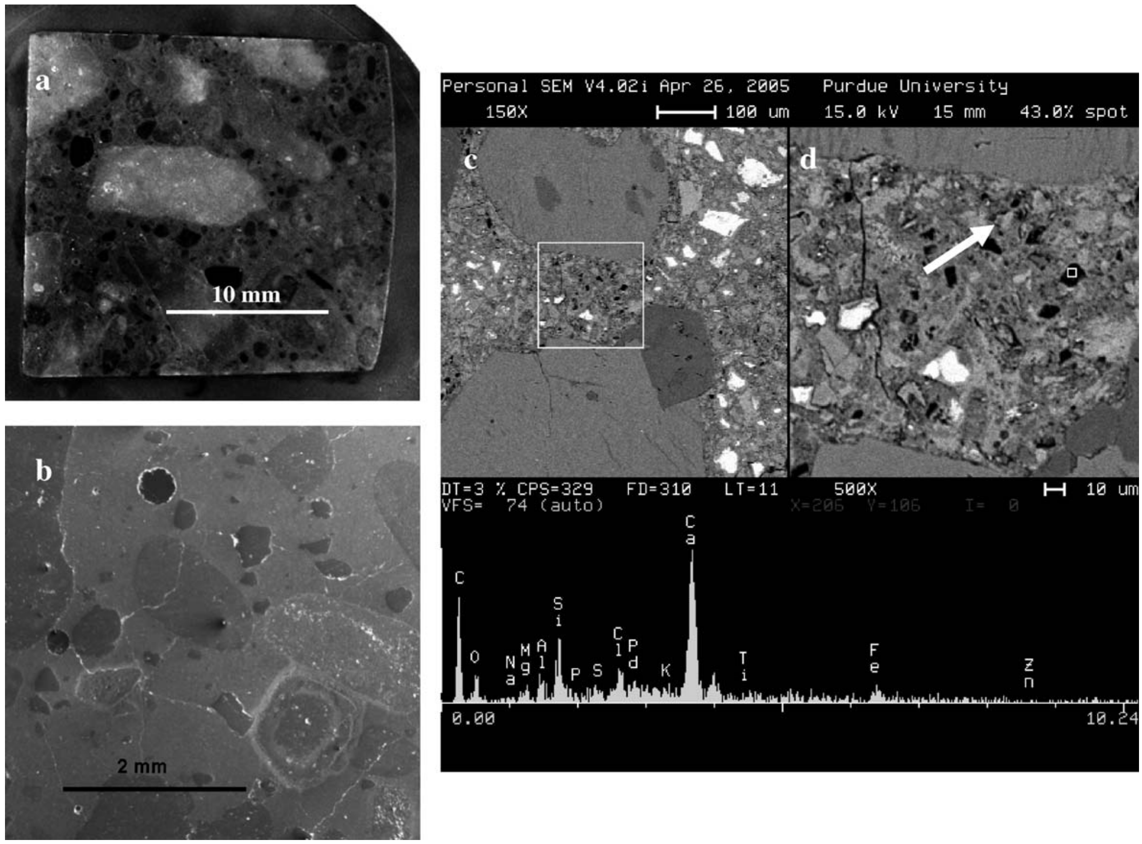

Fig. 1. (a) Appearance of a fully impregnated w:c 0.35 polished concrete specimen. (b) Secondary electron image taken at minimum magnification, showing the flat, fully epoxy-impregnated surface. (c, d) Backscatter SEM showing the patch structure. Note the almost complete absence of unhydrated cement grains in the porous patch, and that the EDS spectrum in the hollow shell pore marked by the white arrow includes C, O, and Cl peaks characteristic of the epoxy resin.

The completeness of the epoxy impregnated layer across the final polished surface is visually evident by the uniformity of the dark color of the cement paste induced by the presence of the epoxy.

Fig. 1 shows a fully impregnated concrete specimen of w:c 0.35, indicating (a) the general appearance of the polished specimen surface, (b) a secondary electron view (at minimum magnification) showing that the surface exhibits almost no relief, and (c) a backscatter SEM image clearly showing the patch structure. With the exception of one or two very large air voids, the entire specimen surface is fully impregnated with epoxy. Thus the argument of Wong and Buenfeld that the alternating dense and porous patches represent alternating areas on the surface of epoxy-filled and epoxy-lacking cement paste is not correct.

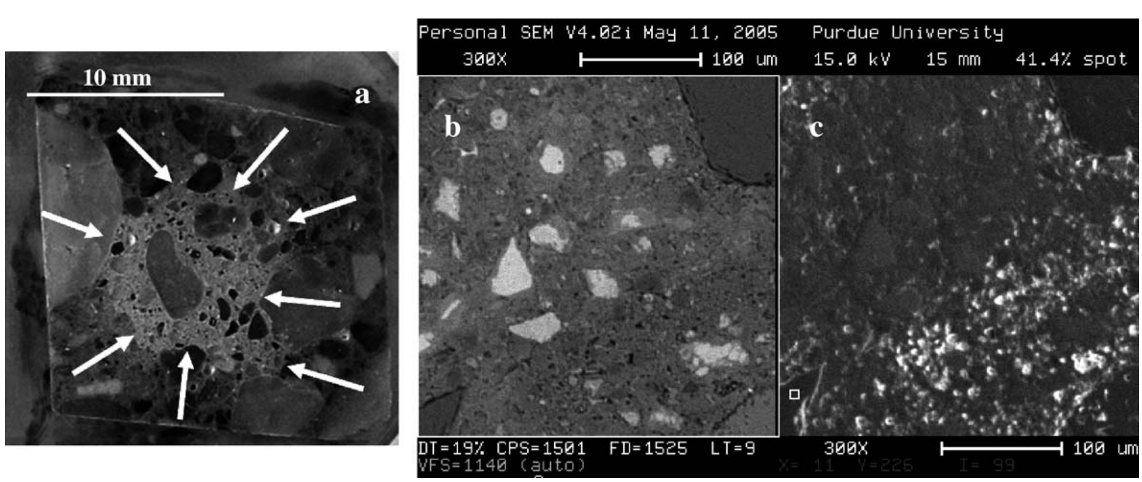

Fig. 2. (a) Incompletely penetrated concrete specimen; white arrows show the limit of epoxy penetration (b) Backscatter image taken within the unimpregnated zone at center of specimen, showing dense patch with unhydrated cement grains and almost no pores (upper left), and porous area almost without unhydrated cement grains (lower right). (c) Secondary electron image confirming that the dense area is in fact dense, and showing the edge brightness of unfilled pores in the porous patch.

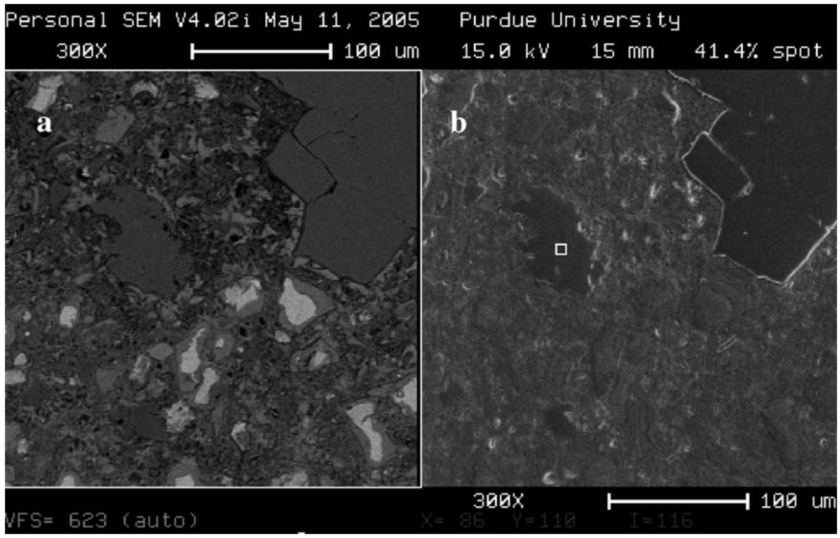

Fig. 3. (a) Backscatter image in a fully impregnated concrete specimen showing dense patch (below, with many unhydrated cement grains) and porous patch (above, almost without unhydrated cement grains). (b) Same area in secondary electron mode. The secondary mode examination confirms that the dense areas are dense: the porous patch shows almost no bright rims, confirming that the pores here are filled with epoxy resin.

Rarely, specimens sliced too deep may show a dark periphery (representing impregnation from the sides) and a light-colored unimpregnated central region. Differences between the impregnated periphery and the unimpregnated center are obvious to the naked eye. In SEM examination the peripheral impregnated areas appear reasonably well polished, and the hollow shell pores within this region provide the distinct EDS signal for the Cl-containing epoxy resin. In contrast, EDS spectra in the unimpregnated core show no indication of Cl, and examination in secondary electron mode shows bright rims around the empty pores.

Fig. 2 shows one of the few incompletely intruded concrete specimens we have produced, a laboratory-mixed concrete of w:c 0.50. The figure includes (a) an overall view of the specimen, showing the obvious distinction between the dark impregnated perimeter and the light-colored core not penetrated by the epoxy, (b) a backscatter SEM image of a typical field within the unimpregnated core, and (c) a secondary electron SEM image of the same area. The backscatter image in this epoxy-free unimpregnated core shows dense and porous patches. The secondary electron image shows that the dense patch areas are clearly and definitely dense. It also shows that the porous patch is in fact porous, displaying the bright edge rims around the pores that provide the characteristic indication of empty pores in the secondary electron SEM mode. Thus the dense and porous patches seen in this entirely epoxy-free core in fact represent the underlying microstructure, not the effect of alternate areas of epoxy-filled and epoxy-empty surfaces.

Fig. 3 is from another w:c 0.5 concrete specimen, similar to the specimen of Fig. 2 except fully intruded across the surface. As seen in (a), the backscatter examination again shows distinct dense and porous areas. Examination of the same area in the secondary electron mode (b) indicates that the dense patch is in fact dense; the pores in the porous patch do not exhibit bright edge rims, since they are filled with epoxy resin.

Images of patch structure in field concretes have been reproduced in some of the writer's publications. These images were taken by the writer from ca. 50 mm epoxy-intruded specimens of concrete that were prepared in the RJ Lee Group, Inc. laboratory, using a different epoxy and a different impregnation procedure. Their procedure is patterned after that described by Jakobsen et al. [2] for fluorescent epoxy-intruded thin sections. The epoxy mix used is Buehler Epoxicure Resin 20-8130 with Buehler 20-8132 hardener, a two-part epoxy mixture to which 1% of Struers Epodye is always added. Drying is carried out to a maximum temperature of 40 °C (slightly higher than the 35 °C described in [2]). Impregnation is carried out under vacuum into a previously ground flat surface. The depth of penetration downward from the prepared surface is typically ca. 150 μm for w:c 0.40 and ca. 1000 μm for w:c 0.6 concretes [2].

Thin sections of 20 μm thickness are carefully prepared to be entirely within this epoxy-filled layer. The completeness and thoroughness of the epoxy penetration throughout the thin section are routinely checked under UV illumination, as required by the standard Nordtest NT Build 361 specification for w:c ratio determination [3]. It is also obvious from the distribution of the yellow color in ordinary light illumination.

The present writer has examined a very large number of specimens of field concrete impregnated in this manner in backscatter SEM, some prepared as well-polished thin sections with a carbon coating added, others as similarly impregnated specimens but polished only on one side. The patch structure is found indifferently in backscatter SEM examination of both kinds of specimens.

Observations of dense and porous patches in optical microscope examinations of fluorescent thin sections were reported as early as 1989 by Idorn [4]. Idorn described the overall w:c 0.45 concrete examined as showing small areas of very dense paste (of seeming w:c ratio of about 0.2) and very porous areas corresponding to much higher w:c. Similar observations are routinely made in examining thin sections by

Thaulow [5] and by others. Idorn [4] considered that the presence of these distinct intermingled patches stemmed from corresponding "compact micropatches alternating with very dilute spaces" pre-existing in the fresh paste before setting. A similar conclusion was drawn recently by Kjellsen [6] who prepared fresh mortar samples, froze them in liquid nitrogen, and then impregnated them fully. Distinct local areas of high concentrations of cement grains were observed, intermingled with areas of much lower concentrations.

Dense and porous patches are thus (1) found in backscatter SEM in fully epoxy-intruded surfaces, (2) revealed by both backscatter and secondary electron SEM in completely unintruded surfaces, and (3) found in both direct light and fluorescent illumination in thin sections. None of these would be possible if the dense patches were in fact due to the artifact in backscatter mode SEM examination alleged by Wong and Buenfeld. On the contrary, the patch structure is an intrinsic and characteristic feature of cement paste in many plain concretes and mortars. A more complete exposition of the evidence briefly described here is being prepared for publication.

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