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The patch microstructure in concrete: Evidence that it exists and is not a backscatter SEM artifact

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Abstract

Many mortars and concretes have been shown by backscatter SEM to contain dense local patches of cement paste exhibiting few detectable pores adjacent to local patches that are highly porous. It has recently been alleged that the dense patches are artifacts induced in backscatter SEM examination in areas insufficiently impregnated with resin. In the present paper we present evidence that these allegations are incorrect. Fully resin-impregnated specimen surfaces show dense and porous patches, as do completely resin-free areas of specimen surfaces. Secondary electron examination in the resin-free areas shows that the porous patches clearly exhibit the rim brightness effects characteristic of empty pores, but the dense patches do not. The boundaries between dense and porous areas may or may not be sharp, and may vary in sharpness even in the same locality. The alleged "artifact" attributed to backscatter SEM is also readily observed in optical microscope thin section examination. Dense and porous patches are also seen in micro-CT examination, which involves no resin and indeed no specimen preparation at all. The patchy structure in hardened concrete appears to originate in corresponding areas of dense and open assemblages of cement grains in fresh concrete.

Keywords: Computed microtomography; Scanning electron microscopy; Microstructure; Hollow shell grains; Mortars; Patch structure

1. Introduction

In several recent publications [1–4] the first-named author has shown that hardened cement paste in various mortars and concretes examined in backscatter-mode scanning electron microscopy (SEM) contains separate dense paste and porous paste areas or patches. Areas identified as dense patches were characterized as often having [1] a high local concentration of large residual unhydrated grains embedded in a dense zone of 'outer product' C–S–H extending over a contiguous area, [2] comparatively few visible pores, and [3] a distinctly bright gray level, indicative of the relative absence of sub-micron pores below the limit of resolution of the SEM. In contrast, areas identified as *porous* patches were seen to show [1] few residual cement grains, [2] a high content of detectable pores, and [3] a generally lower (darker) gray level indicative of extensive contents of sub-micron pores. The detectable pores consist of both hollow-shell hydration grain pores and capillary pores, the latter typically smaller than the former.

In some field concretes (especially those of high w:c ratio that have been subjected to leaching) hydration within the dense patches has removed the unhydrated cement grains, but the obvious porosity differences between dense and porous patches remain.

The sizes of individual patches in different mortars and concretes vary but many are of the order of 150–200 μm. Accordingly, examination at magnifications lower than commonly used in SEM (ca. 100× or 150×) is helpful to recognize their existence. The relative proportions of dense and porous patches varies with w:c ratio. High w:c ratio concretes were found to be mostly porous, only occasional dense patches being present. Conversely, in relatively low w:c mortars and concretes the porous patches are generally

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smaller and tend to be isolated; many of them were found to be associated with sand grains.

Observations of the patchy structures in concretes have not been confined to backscatter SEM; such evidences been found routinely by the second-named author in optical thin section examinations of concrete using visible and fluorescence microscopy. A graphic description of their appearance in optical microscopy was provided some years ago by Idorn [5].

Recently, Wong and Buenfeld [6] and Buenfeld and Wong [7] concluded that the patch structure described above is actually an artifact of backscatter SEM associated with improper specimen preparation. Specifically, they attributed its appearance to irregular impregnation of epoxy resin, suggesting that the dense patches are merely parts of the specimen surface that have been polished beyond the depth of epoxy impregnation. To quote their conclusion from [6] "The appearance of these patches comes from paste areas that have been ground and polished beyond the epoxy resin intrusion depth. In a backscattered electron image, pores not filled with epoxy are not visible because the signal is generated from the base or side walls of the pores."

In the present paper we provide evidence that this conclusion is incorrect, i.e. that the structures in fact exist as described, and we provide an indication of their origin.

2. Illustrations of the patchy structures in concretes

In this section we provide illustrations of the patchy structure as seen in backscatter mode SEM. Fig. 1 provides such an illustration, taken from [4].

In relatively low w:c concretes porous patches are often found to be associated with sand grains. This association, obvious in Fig. 1, is different geometrically from that assumed in the commonly accepted ITZ structure, which also represents an association between pores and sand grains. Porous patches often extend up to several hundred μm into the 'bulk' paste, and may only be in contact with a portion of the surface of a given sand particle. Some sand grains are seen to be completely out of contact with porous areas, but are rather entirely surrounded by and in close contact with dense patches.

Porous patches are also found without visible connection to any sand or aggregate grain. An illustration is provided in Fig. 2, also taken from a 28-day old laboratory concrete. Of course it is possible that the plane imaged is above (or below) a grain that does not intersect the specimen surface.

Fig. 3 illustrates (at very low magnification) the generally patchy character of the paste structure in an

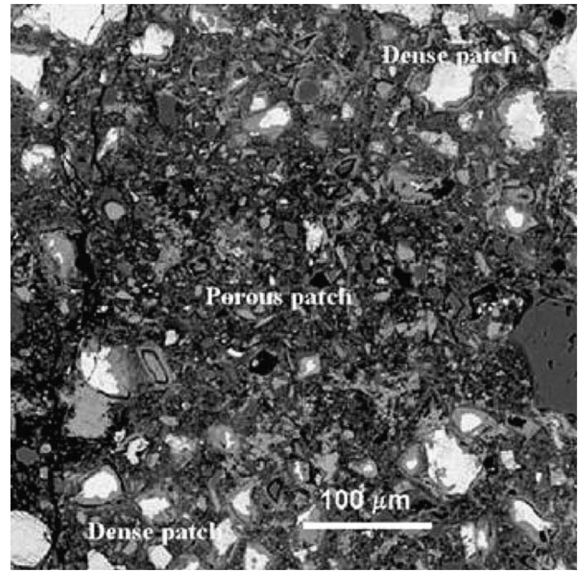

Fig. 2. Porous patch without visible association to sand grains or coarse aggregate.

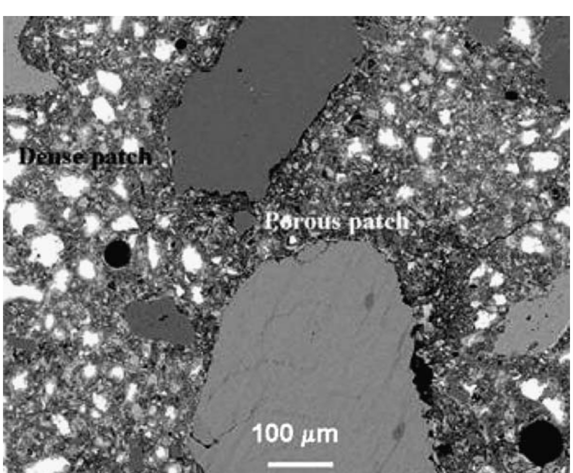

Fig. 1. Backscatter SEM illustration of porous and dense patches in a 28-day old laboratory-mixed w:c 0.50 concrete. Note the virtual absence of the residual cement grains, the many distinct pores, and the darker gray level in the porous patch area.

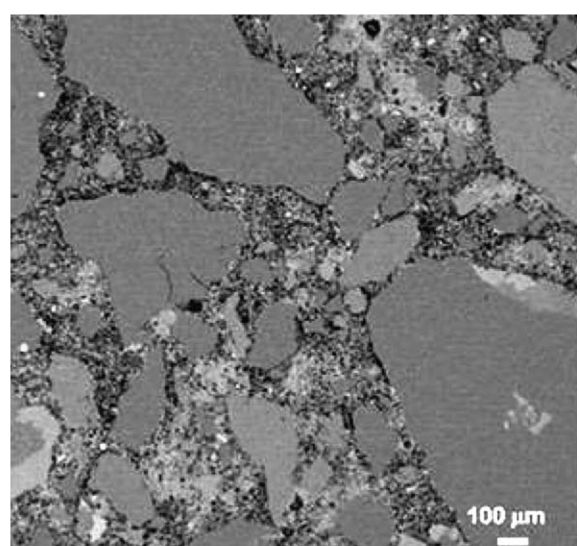

Fig. 3. Low magnification view illustrating the patchy structure observed in a fully hydrated high w:c ratio field concrete.

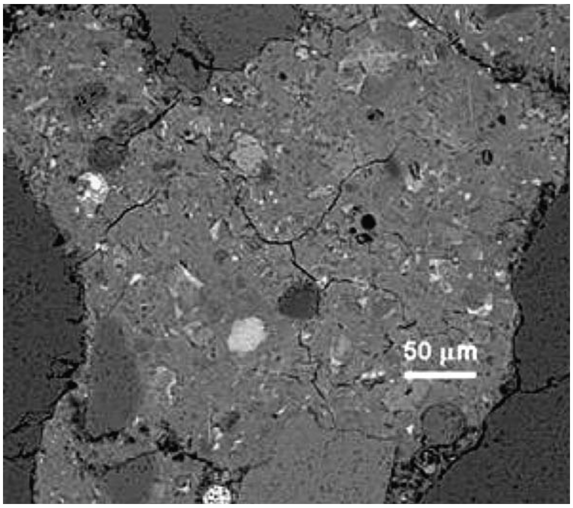

Fig. 4. Higher magnification view of an extensive dense patch in the same concrete specimen shown in Fig. 3.

approximately 8-year old field concrete of w:c ratio estimated at 0.65. The concrete specimen was taken from a slab that has been exposed to ground water and had experienced extensive advection-induced water flow through it. It is seen that dense paste patches are interspersed within a mostly porous paste microstructure.

Fig. 4 provides a higher magnification view of one of the dense patches in the SEM specimen shown in Fig. 3. The dense paste patch illustrated here is seen to extend across the entire space between two widely separated sand grains. Note that since this concrete is almost fully hydrated; residual cement is virtually absent from the porous patches, and the only residual cement grain relics found within the dense paste patch shown are small fragments of C_4AF and occasional bits of β-C_2S. A few fly ash residues are also present. The dense patch here is occupied entirely by dense hydration product, mostly C–S–H.

In the remainder of this paper we discuss the allegations raised by Wong and Buenfeld [6] and Buenfeld and Wong [7] that the features documented here are artifacts of backscatter SEM specimen preparation.

3. Epoxy impregnation in SEM specimen preparation

Since the alleged artifacts are ascribed to the effects of varying presence of epoxy resin in different areas of specimen surface being imaged in backscatter SEM, it is appropriate here to review the nature of the SEM specimen preparation processes in different laboratories.

Many laboratories use some variant of the epoxy impregnation procedure that was developed originally for preparation of thin sections for fluorescent optical examination in the late 1950s, as did Wong and Buenfeld [6].

A common impregnation procedure is to prepare a flat surface, gently dry the specimen and place it in a desiccator, evacuate it, and introduce the freshly mixed epoxy resin over the prepared surface. Penetration is allowed to take place under vacuum for a few minutes, and then atmospheric air is admitted to induce further penetration. The depth of downward penetration of the resin into the surface varies with the pore structure of the sample and with the viscosity of the resin, but it is often not very deep. For example, Jakobsen et al. [8] reported penetration depths of ca. 150 μm for a w:c 0.40 concrete; Kjellsen et al. [9] reported only ca. 120 μm deep penetration into a w:c 0.40 cement paste. Nevertheless, with care it is possible to prepare and polish surface specimens (and to produce thin sections) entirely within the impregnated zone. A laboratory qualified to do the work is essential.

The Araldite AY-103 resin used by Wong and Buenfeld [10] appears to be particularly viscous. Viscosity measurements by the first-named author indicated that Araldite AY-103 resin has a viscosity in excess of 800 cP as mixed, which is two to three times the viscosity measured for other epoxy resins in common use. Thus it is not surprising that conventionally-prepared specimens prepared by these authors may have been polished beyond the depth of penetration in some areas.

These considerations do not apply to the specimen procedure that has been used by the first-named writer at Purdue University for many years. This procedure takes advantage of the unusually low viscosity (ca 60 cP) of a four-component resin developed by Spurr [11]. Unlike many epoxy resins, Spurr's resin does not thicken appreciably at room temperature. This property permits the time allowed for impregnation to be extended indefinitely as desired. The combination of very low viscosity and a long penetration time permits very deep penetration of resin.

In our usual procedure, the specimen is entirely immersed in the resin, and penetration occurs inward from all of the surfaces. Complete penetration often occurs throughout a relatively thick sample prism. In notably impermeable concretes a small volume of material in the center of the prism may remain unintruded, but penetration typically extends at least 5 or 6 mm inward from all surfaces, i.e. downward from the top, upward from the bottom, and inward from the perimeter surfaces. Fig. 5 is a cross-section photograph that shows the penetration

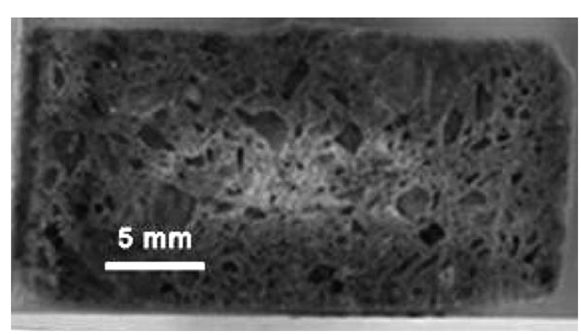

Fig. 5. Sawn cross-section of a w:c 0.40 mortar that was stored underwater for 7 years, and then dried and impregnated, showing the depth of epoxy impregnation from all surfaces. Only the light-colored area in the center is unimpregnated.

attained into an extremely impermeable mortar of w:c ratio 0.40 that had been hydrated under limewater for 7 years. A fluorescent dye (Struer's Epodye) had been added to the freshly mixed epoxy to mark the depth of penetration. The outer 'dark' area (in the black and white reproduction) is actually yellow in ordinary light illumination, and shows the depth of the zone that was penetrated by Spurr's resin.

In our procedure an almost perfectly flat, already fully impregnated surface is obtained by slicing a horizontal surface about 2 mm from the top of the intruded specimen, using a slow-speed wafering saw. The already fully impregnated surface so created is simply ground with fixed diamond plates of successively finer sizes, and finally polished with successively finer diamond pastes down to 1/4 μm in the usual manner.

It is obvious that with such a procedure there is no possibility of inadvertently polishing the surface so that irregular parts of the polished surface extend through the epoxy-impregnated layer so as to create the supposed artifact suggested by Wong and Buenfeld [6] and Buenfeld and Wong [7].

4. Evidence of the existence of the patch structure in both resin-intruded and unintruded areas of backscatter SEM specimens

Fig. 6 shows the normal appearance of a fully impregnated and polished specimen prepared at Purdue University, using the procedure described in the previous section. The polished surface was examined in the secondary electron SEM mode which is sensitive to topographic relief, and found to be almost perfectly smooth even at high magnification.

In a large collection of discarded specimens, two specimens of dense concrete were found in which the cut and polished surface was incorrectly located near the center of the original sample prism, i.e. at a level within the central unintruded area such as that illustrated in Fig. 6. The outer portions of the polished surface of the specimen were impregnated by inward penetration from the perimeter of the prism, as can be seen in Fig. 6, but the central area of the specimen surface was completely unintruded. In Fig. 6 the obvious limit of epoxy penetration from the perimeter is marked by white arrows.

A typical area showing dense and porous patches in backscatter SEM examination of the fully impregnated specimen shown in Fig. 6 is provided in Fig. 7. This figure shows (a) a low-magnification image taken at 150×, (b) a higher magnification of the central part of this area, taken at 500×, and (c) an energy-dispersive X-ray spectrum

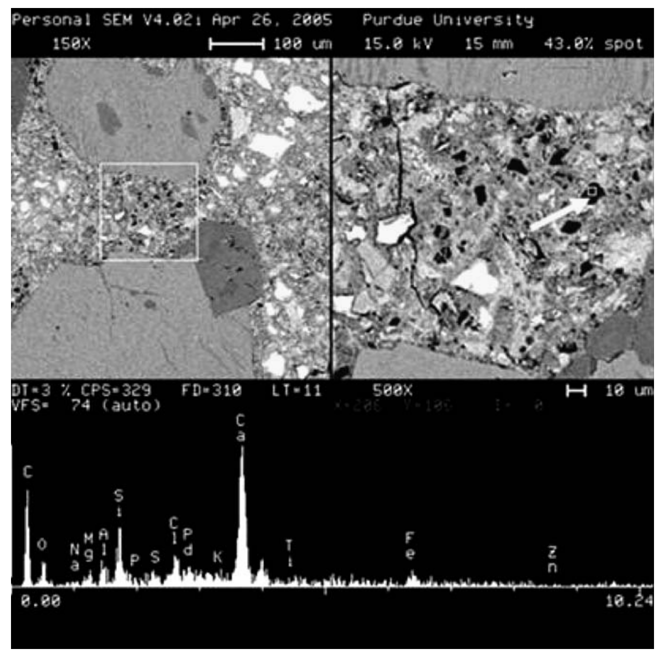

Fig. 7. Backscatter SEM from the fully impregnated specimen shown in Fig. 6. The EDS spectrum is taken from the epoxy-intruded intruded hollow-shell pore marked by the white arrow.

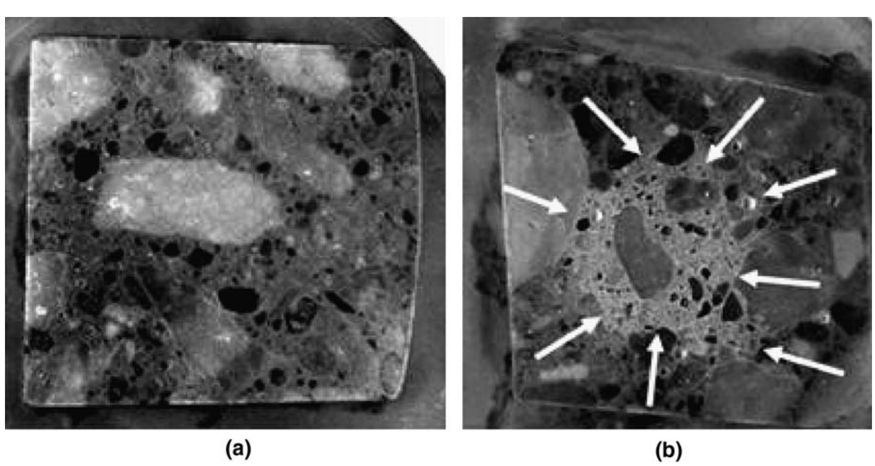

Fig. 6. Appearance of a normal, fully intruded polished specimen surface (left). A discarded specimen whose surface was inadvertently cut below the level of penetration from the top of the original prism. The white arrows mark the limit of epoxy penetration from the perimeter surfaces (right).

(EDS) taken at the location of a hollow shell pore, as marked by the arrow.

The EDS spectrum includes the elemental signature of the resin (C, O, and a weak Cl peak). It is evident that epoxy resin is present. Examination over many areas confirms that the resin is present throughout, although the Cl signal is weaker in some areas than in others. The patch structure is clearly evident in this *fully* resin impregnated surface, and is not an artifact induced by incomplete resin presence at the specimen surface.

Fig. 8 shows two SEM images taken in the entirely *unintruded* central area of the specimen shown in Fig. 6. The left-hand image was taken in backscatter mode SEM. Despite the lack of any resin in the area, dense and porous patches are readily visible. The dense patch occupies most of the upper left two-thirds of the cement paste area shown in the image.

The right-hand image of Fig. 8 shows the same field, but as it appears in the *secondary electron* SEM imaging mode. The secondary electron image confirms that the dense patch is in fact dense; there is almost no indication of pores visible within it. In contrast, the porous patch area in the lower right of the field shows an extensive content of bright edge features, which are characteristic of empty pores intersecting a flat surface in the secondary electron imaging mode. Thus secondary SEM examination confirms that the dense patches seen in backscatter SEM are in fact dense and do not in any way reflect a supposed electron-scattering artifact as alleged by Wong and Buenfeld [6] and Buenfeld and Wong [7].

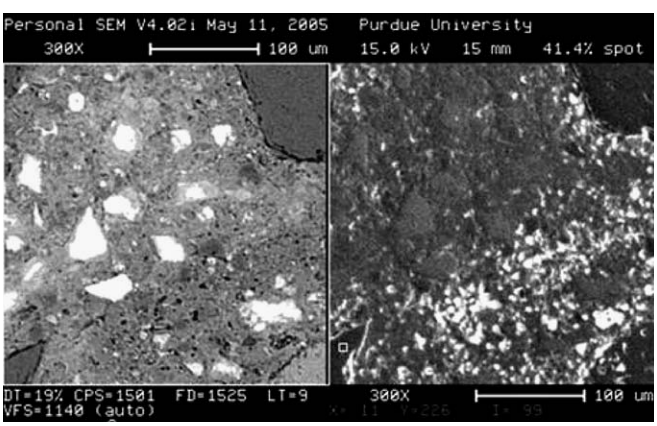

Fig. 8. Backscatter mode SEM image (left) and secondary electron mode image (right) taken in the central unintruded area of the specimen shown in Fig. 7.

In a reply to a discussion of their paper by the first-named author [12], Wong and Buenfeld [13] suggested that in polished surfaces that are locally free of resin "cavities may form bright illumination at their edges or across their entire area, due to charge accumulation. Such bright cavities could be from inherent pores, but also from surface defects such as particle pull-outs, cracks, and surface relief." Extensive examination of the area imaged in Fig. 9 reveal no particle pull outs, no cracks and no local surface relief other than the pores themselves: many of these pores can be identified in backscatter SEM of the same area to be hollow shell hydration grains.

5. Sharpness of boundaries between dense and porous patches

Wong and Buenfeld [13] have suggested that the essence of the patch structure as described by the first-named writer specifically in Refs. [1,14] is the sharpness of the boundaries between the dense and porous areas, i.e. that patches not showing such boundaries are not 'valid' patches. This suggestion is not correct. While sharp boundaries were indeed present in the unusual specimens examined in Ref. [1], the writer remarked in that paper that these sharp boundaries were unexpected, and appeared to be associated with the mixing device used in mixing these mortars. The mixing of these mortars was unusual in that it was done by a modified paint mixer, which applied a purely reciprocating action rather than a rotary action. The writer specifically called attention to previous observations of patch structures in conventionally mixed concretes, and noted that the shearing of the paste under the rotary mixing and the tumbling action may act to blur the sharpness of the boundaries in normally mixed concretes. The second reference cited by Wong and Buenfeld, Ref. [14], was to a "tutorial" paper in microstructure introducing a special issue of

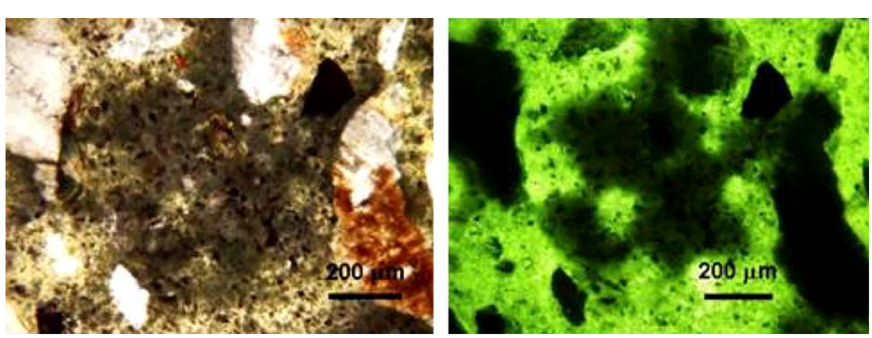

Fig. 9. Illustration of patch structure in a concrete thin section examined in visible light (left) and in fluorescent illumination (right). The central area of the field is a dense patch; the peripheral areas (bright green in the fluorescent image) constitute a surrounding porous patch. A number of sand grains are also present, details of which are seen in the visible light image.

the present Journal; only a very brief discussion of the patch structure was included, with two illustrations. One of the figures was reproduced from Ref. [1]. The other figure, illustrating a normal laboratory mixed concrete, indicated as part of its figure legend that "a sharp boundary occurs at the dashed line; *boundaries in other areas are more diffuse*". The existence of diffuse boundaries in ordinary concrete was also specifically mentioned in the accompanying text.

While fairly sharp boundaries do occur in some places in conventionally mixed concretes and mortars, so do more diffuse boundaries, often in the same general area. It should be quite evident in many of the illustrations provided by the first-named writer in various publications that sharp boundaries between dense and porous areas are not the sine qua non of the patch structure.

6. Patch structure observed in fluorescent optical microscopy

Over a number of years the second-named author has examined several thousand thin sections of mortars and concretes prepared for optical microscope thin section examination in the fluorescent mode. Dense and porous patches have been observed in many of them. A clearly described illustration of dense and porous patches in concrete as seen in optical microscopy was published by Idorn [5] as early as 1991.

Preparation of thin section specimens for such examination has been carefully described by Jakobsen et al. [8]. Impregnation is as previously described for conventional epoxy resin mixes, but the epoxy mix includes a 1% addition of a fluorescent yellow dye (Struer's Epodye). The sample is attached to a glass plate and the free impregnated surface is ground and polished. A precise cut is then made within the impregnated layer to create a new surface parallel to the original polished surface within the impregnated layer, and this second surface is also carefully ground and polished, leaving the thin section at a uniform depth of 20 μm. The fact that the entire thickness of the thin section is fully impregnated with the epoxy is repeatedly checked, first by visual observation of the yellow color induced by the dye, and then by microscopic examination under fluorescent illumination.

Dense paste patches in concrete thin sections are dark in visible light illumination. In fluorescence illumination they show only a low level of the green color induced by the fluorescent-dyed epoxy resin. The high content of residual unhydrated cement grains, where present, is readily seen in the visible light illumination. On the other hand, the porous patches show only few large residual cement grains, and display an intensely green color induced by the fluorescent dye present in the many epoxy-impregnated voids.

Fig. 9 shows a fairly typical concrete specimen as it appears in both visible light illumination (left hand image) and fluorescent illumination (right hand image). In the field examined, the central area is composed mostly of a dense patch, while most of the peripheral area is porous patch. It should be noted that in the fluorescent image care must be taken not to confuse sand grains (easily distinguished in the accompanying visible light image) with dense cement paste patches.

The alleged artifact proposed by Wong and Buenfeld [6] was attributed to a supposed mechanism involving backscattered electron images. In such images it was stated that "pores not filled with epoxy are not visible because the signal is generated from the base or side walls of the pores". The signal referred to is ostensibly created by scattered electrons. That the suggested mechanism is incorrect with respect to backscattered SEM images was shown in Figs. 7 and 8, but in any event it could not possibly apply to optical microscope examination.

7. Specimens prepared at the RJ Lee Group Inc. laboratory

In their reply to the discussion of their paper by the first named writer, Wong and Buenfeld [13] admitted that their suggested artifact would not in fact be expected in specimens prepared at Purdue University with Spurr's resin, but pointed out that images shown in some of the first-named writer's publications were obtained with specimens prepared by the RJ Lee Group Inc. laboratory. They suggested that "there was a high risk that some parts of the sample may be ground beyond the impregnated depth".

In point of fact all such specimens were impregnated with an epoxy resin that is much less viscous than the Araldite AY-103 resin used by Wong and Buenfeld; and all of them incorporated the fluorescent dye. Such specimens are checked routinely for the presence of the dye on all parts of the polished specimen surface. In addition, in backscatter SEM examination of each new specimen in the first-named writer's laboratory the instrumental parameters are routinely set in part by establishing a gray level specifically for epoxy-filled voids. A number of representative voids are specifically examined. In these examinations they are subject to EDS analysis to confirm that they are indeed epoxy filled; the presence of the resin is confirmed by the Cl signal before the gray level adjustment is made. This combination of precautions makes it exceedingly unlikely that these specimens systematically exhibit intermittent local areas of epoxy intruded and unintruded surface in the manner suggested by Wong and Buenfeld [13].

8. Patch structure in micro-CT examination of mortar

Recently, the first named author was provided with the opportunity to examine the results of very well-resolved micro-CT examination of a conventionally mixed mortar carried out by Landis. It was evident that some areas of the mortar contained extensive volumes of dense paste with few pores and high local concentrations of residual unhydrated cement grains, i.e. were dense patches, and other local volumes contained almost no residual cement grains, but large contents of mostly of hollow shell pores, i.e. were porous patches. No specimen preparation was involved in this study except for fracture of the dried mortar to provide a narrow shard for exposure to the synchrotron beam. These findings have been submitted for publication elsewhere [14].

9. Origin of the patch structures

In his perceptive recognition of the patch structure as mentioned previously, Idorn [5] suggested that the patch structure observed was likely inherited from the fresh concrete. In his terms, "This picture shows that the cement paste in its original fresh state has coagulated into very compact micropatches alternating with very diluted spaces".

The idea that dense and porous patches seen in the hardened concrete are derived from corresponding local patches in the fresh state appears to be supported by observations made recently by Kjellsen [15]. Kjellsen prepared several series of mortar specimens which were mixed according to the European cement standard EN 196-1. The freshly mixed mortar specimens were frozen in liquid nitrogen, the frozen water was sublimed off, and the dried fresh mortar was impregnated with epoxy resin and carefully ground and polished. SEM examination revealed the existence in the fresh mortar of distinct areas or patches of high local w:c ratio containing few cement grains, and adjacent areas of low apparent local w:c ratio containing many closely spaced cement grains, in excellent agreement with Idorn's suggestion of "compact micropatches alternating with very dilute spaces" in fresh concretes. These results will be submitted for publication elsewhere.

10. Conclusions

The patch structure that is observed in many mortars and concretes by backscatter SEM exists as such, and is not an artifact of variable penetration of epoxy resin on the polished surface, as was alleged by Wong and Buenfeld [6] and Buenfeld and Wong [7]. The deep penetration of the Spurr's epoxy resin used at Purdue University makes such an eventuality almost inconceivable except in the case of gross error in placing the location of the sawn surface. Specimens that are known to be fully epoxy intruded show the patch structure; so do areas of a specimen surface that has no resin at all. Patch structures have been clearly observed in optical examination of many concrete thin sections, both in visible light and in fluorescent illumination; optical examination is not subject to the electron scattering phenomenon claimed to produce the supposed artifact. Patchy structure has been clearly observed in three dimensions, in a mortar examined in micro-CT, in which no resin intrusion is involved. Indications are provided that the patch structure is derived from pre-existing local structures already present in the fresh concrete.

Acknowledgements

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