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Communication

The patch microstructure in concrete: The effect of superplasticizer

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Abstract

It has been previously shown that laboratory- and field-mixed concretes exhibit dense areas or patches of hardened cement paste (hcp) which are sharply delineated from adjacent, highly porous areas. Direct experiment with long-continued concrete mixing showed that this microstructural pattern is not due to inadequate mixing. An experiment was conducted to determine whether this distinctive microstructure was associated with the flocculation inherent in most fresh concretes. A conventional laboratory concrete was batched and after preliminary mixing a polycarboxylate-type superplasticizer was incorporated. The superplasticizer was added in two successive stages, a modest dose causing some increase in slump, and then a heavy additional dose sufficient to cause complete collapse of slump. SEM examination indicated that the patchy microstructure existed in the 'base' concrete, and was retained in the superplasticized concretes as well. Thus the patchy microstructural pattern is not generated as a consequence of the flocculated state that exists in most fresh concretes.

Keywords: Microstructure (B); SEM (B); Backscattered electron imaging (B); Fresh concrete (A); Superplasticizer (new nomination)

1. Introduction

Evidence has been previously presented [1] that field and laboratory-mixed concretes of water/cement (w/c) ratios of 0.45 or more exhibited a patchy hardened cement paste (hcp) microstructure. Backscatter SEM examination revealed distinct areas (patches) of highly porous hcp intermingled with dense areas displaying little detectable porosity. The dense areas showed a high local concentration of residual unhydrated cement; the porous areas comparatively few. Sharp boundaries between the two types of areas were frequently observed. Similar alternating patches of dense paste and porous paste had previously been detected in laboratory mortars [2] that had been cited some years ago as evidence for the now-conventional model of the interfacial transition zone (ITZ) [3]. It was recently shown [4] that the occurrence of dense and porous patches does not stem from inadequate mixing, since prolonged mixing in an efficient pan mixer did not eliminate it.

An obvious question is whether the effect is associated with the flocculated, that is, undispersed, condition of cement paste in ordinary fresh concretes. Accordingly, a straightforward investigation was carried out to determine whether the dispersion of the cement paste in concrete by incorporating a heavy dose of an efficient superplasticizer would eliminate the occurrence of adjacent dense and porous patches.

2. Materials and methods

A conventional concrete was produced using the same components used in the previously published investigation of the effect of prolonged mixing [4]. These included an ASTM Type I cement, crushed dolomite coarse aggregate, and a local river sand of heterogeneous character. Since a superplasticizer was to be employed, the w/c ratio was reduced from the 0.50 used in the previous investigation to 0.45. As in the previous study [4], the batch volume (39 L) was sized appropriately for the open pan counter-current Lancaster Type SKC mixer used (optimum rated capacity 42 L).

The concrete was initially batched with no admixture and mixed for 4 min using the batching sequence previously described [4]. The mixer was then stopped, the slump was determined, and the 'base' concrete was immediately sampled. A current generation polycarboxylate-type superplasticizer (Glenium™ 3030 NS, a product of the Degussa

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Corporation) was then added in two successive stages. The initial addition corresponded to a dosage of 390 ml/1000 kg. (6 oz./100 lb) of cement, a dosage recommended by the manufacturer for “mid-range use”. After 4 min of additional mixing, the slump of the superplasticized concrete was measured and the concrete again sampled. A second, larger, dose of superplasticizer was then added to the main batch, bringing the total dose to 1170 ml/1000 kg (18 oz/100 lb) of cement. This addition constitutes the upper limit of the dose range recommended by the manufacturer for superplasticizer use. The now heavily superplasticized concrete was mixed for an additional 4 min, the slump again determined, and the concrete again sampled.

The slump of the ‘base’ concrete was 6 cm (2-1/2 in.). It increased to 14 cm (5-1/2 in.) after the first addition of superplasticizer. After the second addition the concrete underwent complete collapse of slump, to a perfectly level fluid surface on the base of the slump test apparatus.

The small samples obtained at each stage were briefly vibrated in open containers, sealed, and cured for 24 h at 23 °C. The containers were then opened, and the samples subjected to 20 days of additional curing in a fog room, again at 23 °C. After curing, thin prisms were sawn from the center portions of each sample using a precision diamond saw and employing a non-aqueous lubricant.

Specimens were prepared for backscatter-SEM examination in the manner normally used in this laboratory. The thin prisms were dried by successive immersions in acetone to remove most of the water, and then placed in an oven for several days at 50 °C prior to epoxy impregnation. The epoxy resin used for impregnation was Spurr’s resin [5], a very low viscosity (62 cP) four-component mixture designed specifically for preparation of electron microscope specimens. This low viscosity resin, unlike many epoxy resins used in various laboratories to impregnate SEM specimens, does not spontaneously gel. It thus can be allowed to continue to penetrate specimens for long periods of time. The impregnation was accomplished by placing each of the specimens in an embedment mold, immersing them in freshly mixed Spurr’s resin, evacuating, and then permitting penetration to occur overnight under continuous evacuation. The impregnated specimens were then hardened at 70 °C overnight. Experience has shown that this procedure provides full penetration through thin specimens of moderate pore connectivity.

The surface to be examined in the SEM was created after impregnation and hardening by slow-speed sawing through the fully impregnated specimen using a precision Buehler wafering saw with propylene glycol as the cooling fluid. The smooth, fully impregnated surface thus created was lapped using 20 cm diameter soft metal lapping wheels containing diamonds of successively finer diamond sizes 45 μm, 30 μm, and 15 μm. The lapped surfaces were then polished using slurries of diamond paste spread on polishing cloth affixed to a slowly rotating 20 cm diameter polishing wheel using diamond pastes of 9, 6, 3, 1, and finally 0.5 μm sizes. The final polished surface was sputter-coated with palladium to provide electrical conductivity.

3. Results

3.1. Microstructure of the ‘base’ concrete

The base concrete exhibited the expected patchy structure, although as expected from the comparatively low w/c ratio used, the proportion of porous patch areas was limited. An area in the base concrete in which several porous patches occur is shown in Fig. 1.

As has been previously observed [1,2,4] the porous patches are relatively dark in backscatter SEM, indicative of the presence of epoxy resin both in resolved pore spaces and in finer unresolved pores. These porous patches contain few unhydrated cement grains. In contrast, the dense areas constituting the majority of the specimen show a distinctly brighter overall gray level and a large complement of closely spaced bright residual unhydrated cement grains.

Porous patch areas were found in many locations in the specimens, but no quantitative assessment of the relative areas was attempted. The focus of this limited investigation was solely to determine if elements of the patch structure existed even in fully superplasticized concrete.

3.2. Microstructure of the moderately superplasticized concrete

Porous patches were readily found to be intermingled with the preponderant dense patch areas in the moderately superplasticized concrete. An example is given as Fig. 2, in which the porous patch occupies the central part of the field. Below it is a dense area with its signature population of unhydrated cement grains; similar dense

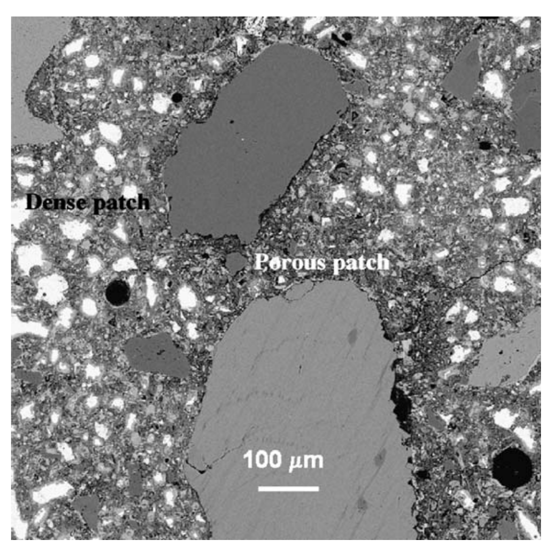

Fig. 1. Low-magnification backscatter SEM showing the characteristic dense and porous patches co-existing in the ‘base’ concrete (w/c 0.45, no admixture, slump 6 cm).

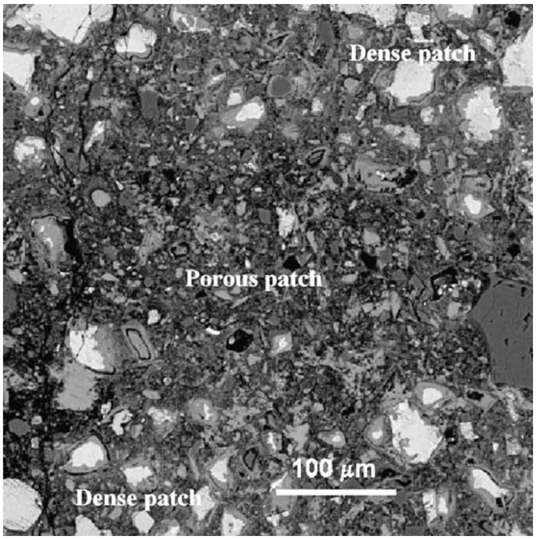

Fig. 2. Backscatter SEM showing a porous patch surrounded by dense patch areas in the moderately superplasticized concrete (w/c 0.45, superplasticizer dosage 390 ml/1000 kg, slump 14 cm).

areas are visible in the upper left and upper right corners of the field. The relatively large porous patch depicted here is not visibly associated with any sand grain, although such grains may have existed above or below the plane of observation.

3.3. Microstructure of the heavily superplasticized concrete

Examination of the heavily superplasticized concrete confirmed that occasional porous patches persisted despite the full dispersion of the cement particles induced by the heavy dosage of superplasticizer and made evident in the complete collapse of the slump behavior. Fig. 3 provides a low-magnification view of a large area in which, as is typical, the dense microstructure predominates, but within which a number of porous patches can be seen. The porous patches appeared to be relatively fewer in number and generally smaller in this heavily superplasticized concrete, but they are definitely present.

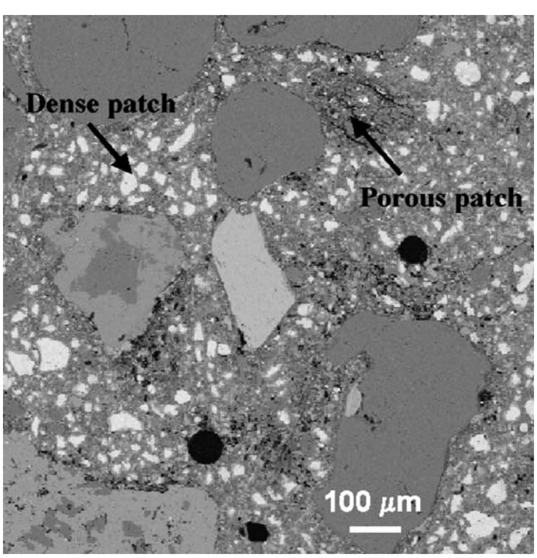

Fig. 3. Low-magnification backscatter SEM showing several small porous patches in preponderantly dense patch areas in the heavily superplasticized concrete (w/c 0.45, superplasticizer dosage 1170 ml/1000 kg, slump collapsed).

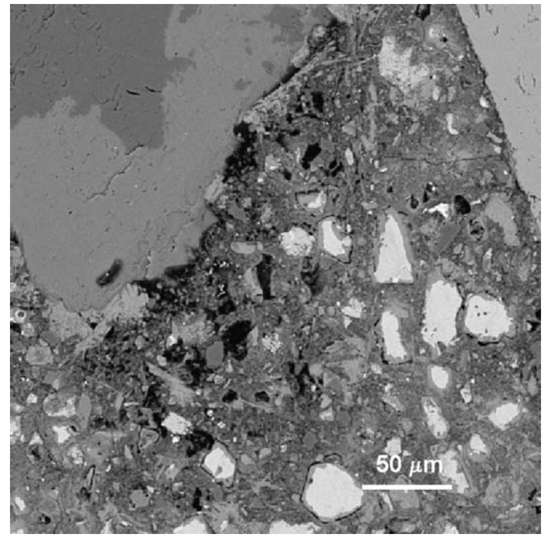

Fig. 4. Enlarged backscatter SEM of an area to the left of center of Fig. 3 showing an almost vertical local boundary between the dense patch to the right and the porous patch to the left.

A portion of this larger area is shown at higher magnification in Fig. 4. The boundary between the dense area on the right and the porous area on the left in Fig. 4 runs almost vertically near the middle of the field.

In Fig. 4, and other areas examined in the heavily superplasticized concrete, it can be seen that some of the visible pores are exceptionally large, and many of them do not have the usual appearance of hollow-shell hydration grains, which are normally the largest pores present. The writer has no explanation for these unusual pores.

4. Conclusions

1. The patchy microstructure, comprising dense areas exhibiting a high concentration of residual unhydrated cement grains interspersed with highly porous areas with almost no residual unhydrated cement grains is found to persist in a laboratory-mixed concrete so heavily superplasticized that that complete collapse of slump was observed.
2. Thus it is concluded that the patchy structure is not produced as a consequence of the flocculated condition of the cement paste in conventional fresh concrete.

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