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THE OCCURRENCE OF TWO-TONE STRUCTURES IN ROOM-TEMPERATURE CURED CEMENT PASTES

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ABSTRACT

It is generally accepted that high-temperature steam cured concretes, or concretes otherwise exposed to high temperatures during early hydration, can be recognized by the subsequent presence of "temperature relics" in the form of banded or layered hydration rims displaying two-tone or sometimes three-tone appearance in backscatter SEM. We have found (and illustrate) populations of such supposed indicators of high-temperature curing in various small specimens that have been cured entirely at room temperature. Accordingly, we suggest that such banded structures may arise in other ways, and their presence does not necessarily indicate that high-temperature curing has occurred. *© 1998 Elsevier Science Ltd*

Introduction

In recent years microstructural investigations on cement systems have concentrated heavily on backscatter SEM imaging of plane polished surfaces, usually of epoxy-impregnated specimens. Such images are frequently rich in detail, and important information can readily be detected and described. However, interpretation the features observed is not necessarily straightforward and is subject to the usual uncertainties underlying scientific investigation.

Some years ago widespread failures in steam-cured concretes, particularly railroad ties, began to engage the attention of the concrete technical community. The failures were at least partly induced by delayed ettringite formation (DEF), which has since become a subject of major concern. It is widely accepted that many DEF problems are associated with steam curing at excessively high temperature. Accordingly, internal evidence relating to whether a given concrete had or had not been cured at excessively high temperature has been sought by various investigators.

Scrivener (1) described the results of experiments in which small specimens of cement pastes were hydrated for 4 h at 20°C, then progressively heated to 80°C over 4 h, maintained at 80°C for 16 h, cooled, and then maintained at 20° for various periods of further hydration. She observed formation of so-called "two-tone" inner product features after 35 days of hydration following the high temperature treatment.

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In backscatter SEM the inner product appears as a band of relatively dense C-S-H formed directly around, and usually in contact with, a bright residual unhydrated core of the clinker grain. These distinct features are described as hydrated phenograins in the nomenclature of Diamond and Bonen (2). In smaller grains, especially in well-hydrated pastes, the entire grain may be hydrated and the bright unhydrated core absent.

In Scrivener's report the "two-tone" character comprised a brighter outer band thought to be formed at 80°C and a darker inner band considered to be formed on subsequent exposure at 20°C. The latter was reported as increasing in thickness with progressive hydration. No description was provided in her brief note of the appearance of companion pastes not subject to heat treatment.

Clark et al. (3), in a paper presented in 1992, indicated that such two-tone relics could be found in concrete steam cured to high temperatures of 80°C and 100°C, but not to concrete steam cured to 60° or to concrete cured continuously at 20°. These authors also reported the occasional occurrence of three-tone features. With respect to either two-tone or three-tone features, they concluded that "Such microstructures were never observed in samples cured at ambient temperature, thus are believed to be the result of the curing procedure." Subsequently further observations of two-tone and multiple-tone features in high-temperature cured concretes were reported from the same laboratory in a paper by Jie et al. (4).

Accordingly, various investigators have relied on the occurrence of two-tone relics in a given concrete as a primary indication that the concrete had undergone high temperature steam curing.

In this paper we report the presence of similar two-tone banded structures in cement pastes prepared and hydrated under conditions in the laboratory which do not include exposure to temperatures other than laboratory ambient temperature (approximately 23°C).

Experimental

Several cement pastes that had been prepared for other purposes were examined by backscatter SEM specifically to provide illustrations of two-tone relicts, which had been observed previously on a casual basis. All of the specimens were prepared in the normal manner used to prepare backscatter SEM specimens in this laboratory. The procedure involved several steps. Thin (ca. 5 mm thick) slices of pastes were prepared and immersed in acetone for approximately 6 h to remove most of the water by solvent exchange. The specimens were then exposed to vacuum in an evacuated desiccator for 3 h at room temperature to remove most of the acetone. The specimens were then oven dried at 105° C for 8 h to remove any remaining traces of water or acetone. They were then cooled to room temperature and immersed in Spurr's ultra low viscosity resin mix under vacuum at room temperature for several hours. The impregnated resin was hardened by exposure at 70°C for 2 h. The specimens were then sliced with a low-speed diamond saw to expose a fresh plane surface to be examined. This newly-exposed surface was then ground and polished with successively finer grades of diamond grit, and lightly sputter-coated with a gold-palladium alloy.

The specimens were examined at 15 KeV using an Akashi Beam Technology 55A SEM equipped with a GW Electronics split-quadrant backscatter detector. The micrographs reproduced in this paper were all taken at a uniform original magnification of 500x.

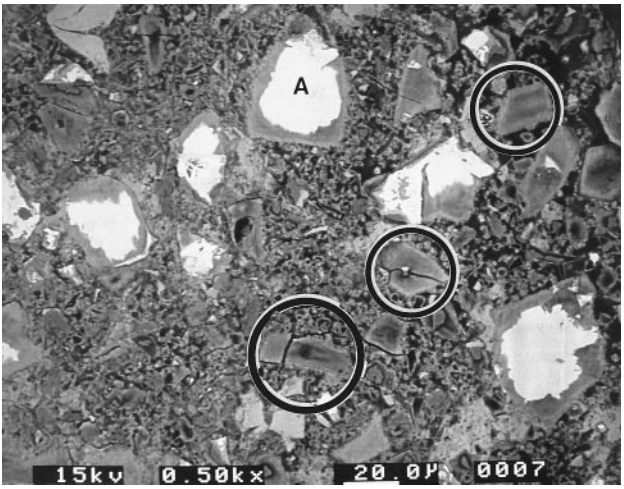

FIG. 1.
SEM from room-temperature cured 100-day old plain Portland cement paste showing two-tone grains.

Results for 100-Day Old Plain Portland Cement Paste

This paste was a normal Portland cement paste prepared from a normal commercial Type I cement of relatively low alkali content (0.46%, mostly as K_2O) and moderate sulfate content (2.66% SO_3). The potential compound composition (standard Bogue calculation) was 70.0% C_3S, 13.5% C_2S, 10.9% C_3A, and 6.3% "C_4AF."

The paste was mixed at a w/c ratio of 0.45 in a Hobart mixer in strict conformity to ASTM C-305. After mixing it was placed in a plastic ointment jar, sealed, stored for 1 day, demolded, and stored in a saturated lime water solution for 100 days at ambient laboratory temperature.

Figures 1 and 2 are taken from different areas on the polished surface. In this paste most of the clinker grains smaller than about 25 μm are completely hydrated; most of the larger cement grains are only partly hydrated, and show bright inner cores of unhydrated clinker surrounded by hydrated rims.

Figure 1 contains evidence of two-tone structure in both fully hydrated and partly hydrated grains. Three of the former are circled for easy recognition. The ca. 40 μm grain marked A in the upper part of the field is only modestly hydrated, but also reveals the two-tone character in its relatively narrow rim.

As indicated originally by Scrivener (1) for two-tone features in heat-treated pastes, the outer portions of these structures are lighter colored than the inner portions. In the present figure there an occasional tendency toward development of a three-tone structure, as can be seen in the circled grain in the upper right portion of the figure.

Two of the circled features in Figure 1 display cracks running entirely across them. Cracking across such features was displayed in heat-treated samples in the papers by Clark et al. (4, Fig. 9) and by Jie et al (2, Fig. 7). On the other hand, in this paste most individual two-tone features are not cracked, and the cracking may be of little significance.

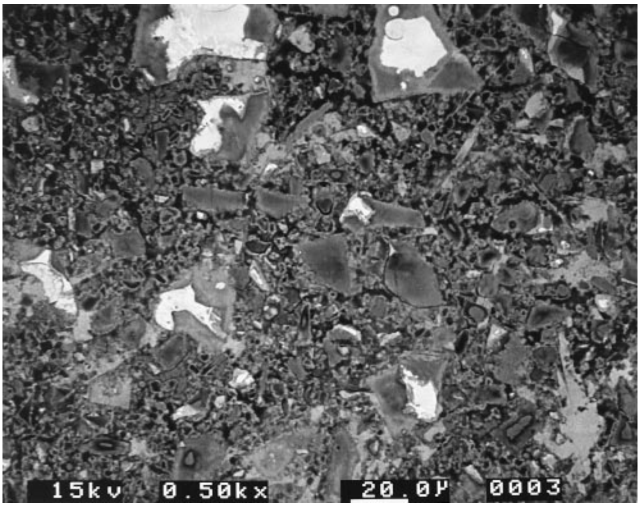

FIG. 2.
SEM from room-temperature cured 100-day old plain Portland cement paste showing two-tone grains.

The prevalence of two-tone grains in this paste is well illustrated in Figure 2, which contains a large number of smaller fully hydrated grains. The two-tone character is present in virtually all of them.

Results for 100-Day Old Silica-Fume-Bearing Portland Cement Pastes

This paste was prepared using the same cement and water:binder ratio as above, but 10% of the cement was replaced by an equal weight of commercial silica fume. No superplasticizer was used. The mixing and storage procedures were identical to those used for the plain paste.

Scanning micrographs from two widely separated areas are shown as Figures 3 and 4.

In Figure 3, it appears that while incorporation of the silica fume has led to some modifications of the microstructure, the two-tone features are prominent in this paste as well. Again the larger residual cement grains show unhydrated cores, and most of the smaller ones do not.

The two-tone structures exhibited here are even more distinct than those exhibited in Figures 1 and 2, in that the gray levels of the separate zones are more sharply distinct from each other. In the plain cement paste depicted in Figures 1 and 2 there appears to be more of a tendency for gray levels of the separate zones to grade into each other.

Some of the occasional uniform gray grains found in paste shown in Figure 3, for example that in the upper right corner of the field, appear to represent undispersed silica fume agglomerations, as described by Bonen and Diamond (5) and many others.

Figure 4, from another area of the silica fume-bearing paste shows similar features. In particular, it includes two of large grains with substantial unhydrated cores, that nevertheless show the two-tone feature in their hydration rims. These are marked “B” and “C.” Fully hydration grains with two-tone structure are also visible.

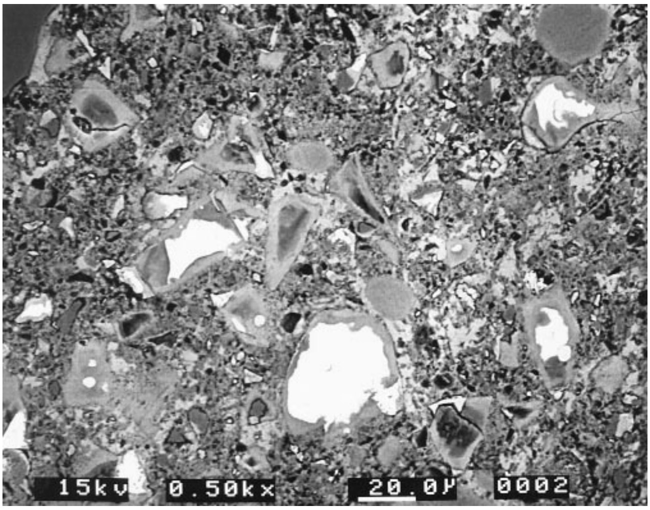

FIG. 3.
SEM from never room-temperature cured 100-day old silica fume-bearing portland cement paste showing two-tone grains. Note the sharp boundaries between zones of different tone.

Results for 24-Year-Old Plain Cement Paste

This plain portland cement paste was prepared in 1972 by Professor D. N. Winslow at Purdue University. The paste was mixed at a w/c ratio of 0.40 in air, never heated, and was stored in saturated lime water continuously since that time.

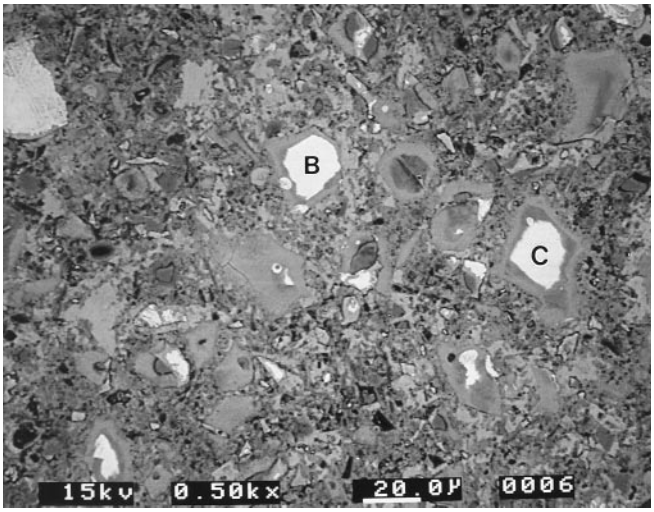

FIG. 4.
SEM from room-temperature cured 100-day old silica fume-bearing Portland cement paste showing two-tone grains.

Figure 5 shows a typical field.

As would be expected for a 24-year-old paste cured in water, essentially all of the clinker grains are fully hydrated. One would not expect to find grains like “B” and “C” in Figure 4 in the previous paste to be present here.

The various fully-hydrated grains appear to show more variation in the tonal pattern than was present in the previous pastes. It appears that multi-toned grains rather than simple two-toned grains constitute the majority of the grains present.

Discussion

Some question may arise as to whether the brief exposure to oven-drying after acetone exchange of these mature specimens could have induced the two-toned and multi-toned structures depicted. This appears not to be the case. A specimen of the 24-year-old paste was prepared entirely without oven drying or resin impregnation and polished from the original condition. As might be expected, only an indifferent surface could be achieved, but SEM examination did confirm the presence of two-tone relics in this surface.

Scrivener (1), Clark et al. (3), and Jie et al. (4) have clearly shown that two toned (or multi-toned) relics can be induced by high temperature heating, and according to Clark et al., two-tone features were not found in samples cured at 60°C or in samples hydrated at room temperature.

We have no explanation for the fact that two-toned structures are sometimes encountered in room-temperature cured pastes but not in many others. As indicated previously, the cements used, mixing procedures, and room temperature curing procedures used here were normal. Many room-temperature cured cement pastes and concretes have been examined by the first-named author and his colleagues, and of course by many other workers. The

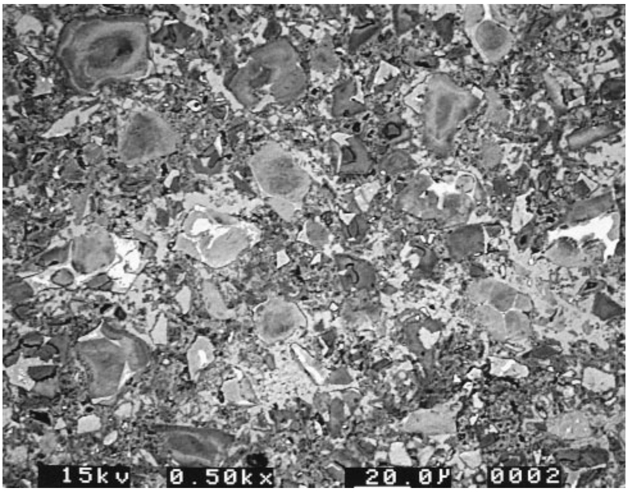

FIG. 5.

SEM from room-temperature cured 24-year-old Portland cement paste showing two-tone grains occurrence of two-toned banded structures has not been generally observed, or at least have not been displayed prominently enough to elicit specific mention.

Nevertheless, the present results indicate that the range of circumstances that induce or encourage formation of two-toned structures, while including high temperature steam curing, are not confined to such curing. Accordingly, it appears that the presence of such structures in pastes or concretes is not in itself proof that the paste or concrete in which they are found has been exposed to high temperature curing.

Conclusion

Two-toned (and multi-toned) hydration rim “relics” are shown to sometimes occur as prominent features in cement pastes (and presumably in concretes) that have never been exposed to heat treatment. Thus the use of the presence of such features in a given concrete as definitive evidence that the particular concrete has been steam cured at high temperature may be subject to question.

Acknowledgments

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