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Scanning electron microscopic investigations of fresh mortars: Well-defined water-filled layers adjacent to sand grains

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Abstract

SEM examinations are reported of freshly-mixed and early age mortar specimens prepared by fast freezing in liquid nitrogen followed by epoxy impregnation, and of companion specimens of early aged mortars prepared conventionally. Freshly-mixed mortars reveal complex features that appear to influence subsequent development of the hardened state microstructure. In particular, layers of entirely water-filled space a few micrometers thick are found adjacent to many of the sand grain surfaces. After a few hours sparse deposits of calcium hydroxide crystals (and later C–S–H) are found within these layers, but the layers persist as recognizable features for at least 12 h. The layers are identically recognizable in both fast-frozen and conventionally-prepared specimens. Another feature found in freshly-mixed mortars is the existence of patchy local areas of sparsely-packed and other areas of densely-packed cement particles.

Keywords: Fresh mortar; Microstructure; Water-filled layers; Fast freezing; Cement particle arrangements

1. Introduction

The microstructural arrangements of cement grains in the spaces around (and between) aggregates in fresh concrete collectively constitute the skeleton on which hardened concretes develop. Despite the importance of accurate information on the initial state of the concrete skeleton, few results of direct examinations of fresh concretes or mortars exist, although various authors have reported microstructural studies on cement pastes without aggregates.

A study of fresh mortar was reported some years ago by Escadeillas and Maso [1]. These authors attempted to preserve the structure by freezing large mortar samples contained in 20-mm diameter plastic test tubes in liquid nitrogen. However, freezing rates for such large specimens are necessarily slow, and formation of large ice crystals may well have altered the particle arrangements in the mortars.

The present writers have carried out backscatter scanning electron microscope (SEM) observations on a series of fresh (and early age) laboratory-mixed mortars, starting with specimens prepared immediately after mixing, and continuing at subsequent intervals during setting and hardening. In a recent paper [2] we reported a number of the observations made with respect to the arrangements of cement particles in fresh mortars, including in particular our confirmation that local densely-packed zones and highly porous patches existed in the fresh mortars. In the present paper we describe and illustrate our findings that extensive and geometrically sharply-defined layers of what appear to be water-filled spaces entirely free of cement particles occur adjacent to many of the surfaces of sand grains. These water-filled layers appear to provide areas adjacent to aggregate surfaces within which layered deposits of calcium hydroxide (CH) are subsequently precipitated. Such layered CH deposits on aggregate surfaces are a well-established feature of hardened mortars and concretes. Their existence was originally documented many years ago [3], and they have been subsequently described by many authors, including Scrivener and Pratt [4], Bonen [5], Kjellsen et al. [6], and Diamond [7].

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2. Experimental details

2.1. General features of specimen preparation

As indicated earlier, microscopic observations of the local grain-to-grain arrangements in fresh mortars have not been commonly reported, primarily because of the difficulty of preparing fresh mortar or concrete specimens for such observation without appreciably altering their pre-existing grain-to-grain arrangements. In this work we employed a technique described in several previous publications [8,9]. This procedure involved epoxy impregnation and polishing of very small fragile specimens of fresh or early aged mortars after water had been removed by prolonged low-temperature sublimation after fast freezing in liquid nitrogen.

Many studies have been reported on the effects of fast freezing on biological tissues, which are usually examined in thin sections at high magnifications of ca. 15,000×. Such studies suggest that even with very fast freezing under high pressure, it is difficult to always avoid the generation of fine ice crystals [10]. Such crystals have been shown to pierce the tissues and disrupt the fine details of the tissue structures [11]. Formation of fine ice crystals would not necessarily influence the grain-to-grain arrangements of cement and sand grains in fresh mortars since cement particles are much more massive than the features observed in biological tissues. Nevertheless the possibility of some alteration of the initial grain-to-grain arrangements and of the details of the early hydration product must always be considered.

Such concerns led to the preparation of ‘control’ specimens from some of the present mortar mixes. Control specimens were prepared using a conventional SEM specimen procedure involving immersion in ethanol for 2 days to remove much of the water, then drying at 60 °C for 2 additional days. This was followed by the epoxy impregnation and polishing procedures normally carried out for backscatter SEM observations of hardened cement systems. Such ‘control’ specimens were not attempted for freshly-mixed mortars because of the likely changes in particle arrangements induced on drying freshly-mixed mortars, but were found to be practical and useful for comparison of specimens of early age mortars 6 h old and older.

Comparison of features found in the two types of specimens produced from the same mortar at 6 and 12 h indicated that the microstructural features were very much the same, i.e. that significant freezing-induced microstructural alterations were absent [2]. The grain-to-grain arrangements found in both control mortars and fast-frozen mortars at 6 h were basically identical to those found in the fast-frozen freshly-mixed mortars, with an exception to be discussed later. Thus it was concluded that in fast freezing and low-temperature subliming the freshly-mixed mortars, we were generally able to preserve the essential features of their grain-to-grain arrangements.

2.2. Materials, mixing, and curing procedures used

Table 1
Composition of the mortars, grams per batch

w:c ratio	0.25	0.40	0.50
Cement	650	515	450
Sand	1350	1350	1350
Water[a]	163	205	225
Superplasticizer	22.8	3	–

[a] Total water, including water in superplasticizer.

A Swedish low-alkali sulfate resistant cement (equivalent to an ASTM Type V cement) was used. The mill analysis gave the following percentages by weight: 22.3% SiO_2, 3.3% Al_2O_3, 4.6% Fe_2O_3, 64.3% CaO, 0.85% MgO, 0.56% K_2O, 0.17% Na_2O, 2.3% SO_3, and 0.71% ignition loss. The Blaine specific surface areas and density were given as 309 m^2/kg and 3220 kg/m^2, respectively.

Mortars were prepared at three w/c ratios: 0.25, 0.40, and 0.50. All of the mortars were batched at the same paste volume of 42%. The sand was a reference silica sand, CEN silica sand as specified in the EN 196-1 European standard. A single bag (1350 g) of this sand was used for each mix batch.

A modest dose of naphthalene sulfonate-based superplasticizer was necessary to obtain appropriate fluidity for the w/c 0.40 mortar, and a much higher dose for the w/c 0.25 mortar.

The batch compositions for the mortars of the different w:c ratios are provided in Table 1.

Mixing was carried out according to the European Standard EN 196-1, Part 1, Methods of Testing Cement, which involved final mixing for 1 min. However, a second, more extensively mixed w:c 0.40 mortar batch was also prepared to check the possible effect of more extended mixing; the duration of the final mix sequence for this one was 2 min instead of the 1 min specified in the standard method.

For each mortar a small, ca. 0.25 g sample, was obtained for fast freezing immediately after mixing. The remainder of the batch was placed in a mold and conditioned as prescribed in EN 196-1, at approximately 20 °C room temperature and 100% RH. Early age mortar samples were taken and specimens were prepared for SEM examination at 6 and 12 h of hydration, and mature mortar samples prepared after 28 days.

2.3. Specimen preparation and SEM examination procedures

Specimen preparation, especially of the freshly-mixed mortars, is obviously the most critical step in these investigations. On one hand, in fast freezing, the smaller the specimen, the faster the freezing occurs, and the less the likelihood of developing detectable ice formation artifacts. On the other hand, specimens of appreciable size are needed to obtain a representative volume of the mortar for examination in different areas. The sample size selected, approximately 0.25 g, was a reasonable compromise, but as discussed later, in a few of the specimens indications of possible ice crystal formation were found.

The specimens were taken without reference to any particular spatial orientation.

Mortar samples of approximately 0.25 g were taken immediately after mixing and after predetermined periods, and were quenched in liquid nitrogen. They were then subjected to low-temperature sublimation at pressures between ca. 10^{-4} and 10^{-2} Mbar. In the ice–water vapor phase diagram, these pressures correspond to temperatures between ca. −90 °C and −60 °C. Sublimation was continued for a three day period, which resulted in essentially complete removal of the frozen mix water.

The sublimed specimens were exceedingly fragile and extremely careful handling was required to successfully impregnate and polish them for SEM examination. The epoxy resin used was Epo-Tec 301. After impregnation the impregnated specimens were hardened, carefully polished and carbon coated. Before the backscatter examinations, each of the polished specimens was examined in secondary-mode SEM to check that they were flat and fully impregnated with epoxy resin.

The backscatter SEM examinations were carried out with a Hitachi S-4300 Field-Emission SEM, with the accelerating voltage being maintained at 10 keV throughout. A number of areas of each specimen were examined to be certain that the images obtained were representative. In all, approximately 320 backscatter SEM images were produced in this study.

3. Results of examinations

3.1. Observations on specimens fast-frozen immediately after mixing

A representative image of a w/c ratio 0.25 mortar specimen prepared by freeze-drying immediately after mixing is shown as Fig. 1. The Portland cement particles are white, and can be easily distinguished from the gray sand grains by their brightness. The black areas represent originally water-filled spaces from which the water was removed by sublimation and subsequently replaced by epoxy resin.

We call attention to the lack of cracking or other visible effects of the fast freezing and subsequent ice sublimation processes in Fig. 1.

The reader's attention is directed to two specific features in the figure. One is the distinction between the dense local population of larger cement particles in the paste to the left of the sand grain in the center of the field, as compared to the sparse population of such grains to the right of the sand grain. This is an obvious example of the patchy local variation in fresh paste of concrete originally postulated by Idorn [12] and illustrated in a previous paper by the present authors [2].

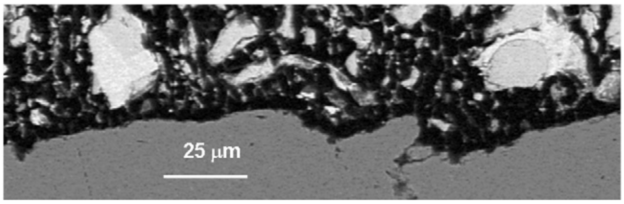

Fig. 2. Enlarged area above the large sand grain of Fig. 1.

However, the feature found in Fig. 1 that constitutes the principal focus of the present paper is the presence of a distinct epoxy-filled continuous black layer about 3 μm thick immediately adjacent to many of the sand grain surfaces. Such a layer extends notably along the surface of the large sand grain that stretches across the entire field in Fig. 1. This feature has been found in all fresh mortar specimens and also in all of the early age specimens, both conventionally-dried and fast-frozen. It is considered that the epoxy-filled layers replace originally water-filled layers in the same locations.

Fig. 2 shows the central area just above the large sand grain at the bottom of Fig. 1; enlarged to show this feature more clearly.

It is seen that the outline of the black layer follows the local convolutions of the sand grain surface with considerable fidelity. A population of various small particles can be seen above the epoxy-filled black layer, including cement particles of appreciable size as well as micrometer-sized cement particle 'chips', and also μm or sub-μm sized gray particles. The gray particles appear to be immediate products of hydration from some of the fine cement chips. Both white cement particles and gray particles are notably absent within the black epoxy-filled layer adjacent to the sand grain.

Fig. 3 was obtained from the freshly-mixed w/c 0.50 mortar specimen.

Large cement particles, many 50 μm or more in size, are concentrated noticeably in the lower right quadrant of the field. In contrast the paste between two sand grains in the upper left of the field has few such particles.

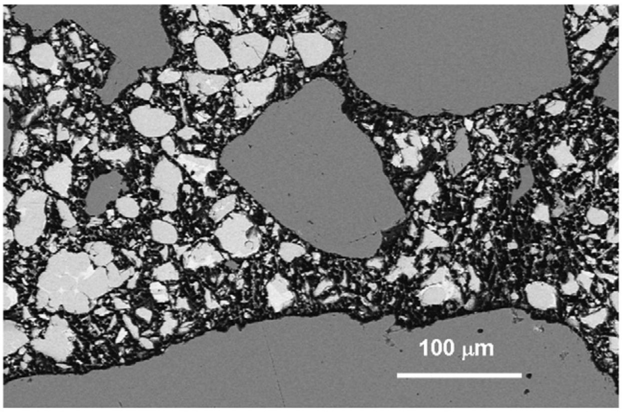

Fig. 1. SEM image of w/c 0.25 mortar fast-frozen immediately after mixing.

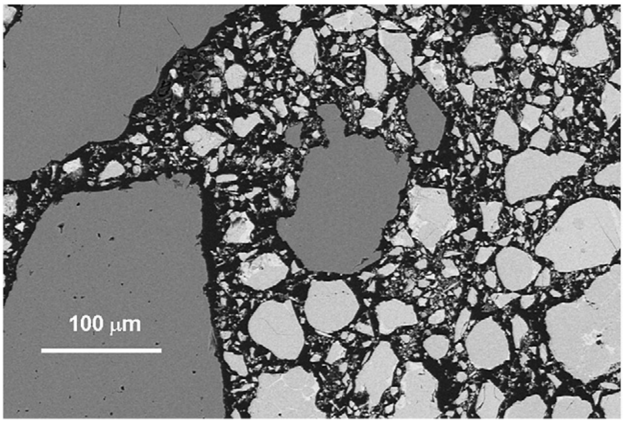

Fig. 3. SEM image of w/c 0.50 mortar fast-frozen immediately after mixing.

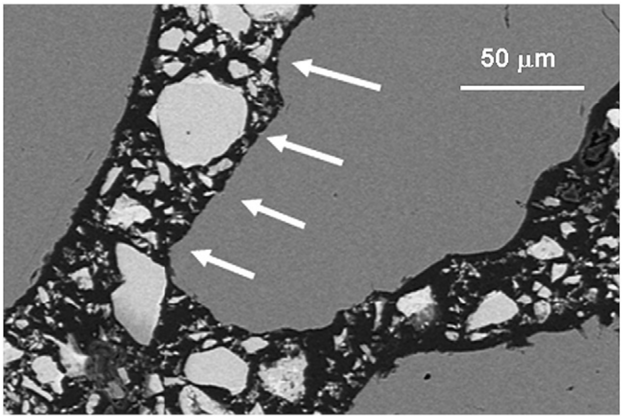

Fig. 4. Area to the left of Fig. 3 showing the incompleteness of the particle-free black layer around a particular sand grain.

Black epoxy-filled layers such as were seen in Fig. 2 are also seen here, particularly around the two larger sand grains at the left of the field. Thus Fig. 3, from a freshly-mixed w/c 0.50 mortar displays both of the features pointed out in Fig. 1 for a freshly-mixed w/c 0.25 mortar.

It may be recalled that the w/c 0.25 mortar shown in Figs. 1 and 2 contained a heavy dose of superplasticizer; but that none was incorporated in the w/c 0.50 mortar of Fig. 3. Thus neither the local patch structure nor the presence of the water-filled black layers around aggregate surfaces is associated with the presence or absence of superplasticizer.

In Fig. 3 it is seen that some areas around sand grains do not have fully-developed black layers free of cement particles. This is illustrated specifically in Fig. 4, taken from an area just to the left of Fig. 3. The white arrows indicate a part of the sand grain perimeter where some cement particles are in fairly close contact with the sand grain surface, and a particle-free intervening water-filled layer is locally absent.

3.2. Observations on early age fast-frozen and conventionally-dried mortar specimens

It was previously mentioned that 'control' specimens were prepared for early aged (6 and 12-h old) w/c 0.40 mortars using conventional drying so as to provide comparisons with the corresponding fast-frozen specimens. Figs. 5 and 6 illustrate such a comparison for 6-h old w/c 0.40 mortar specimens.

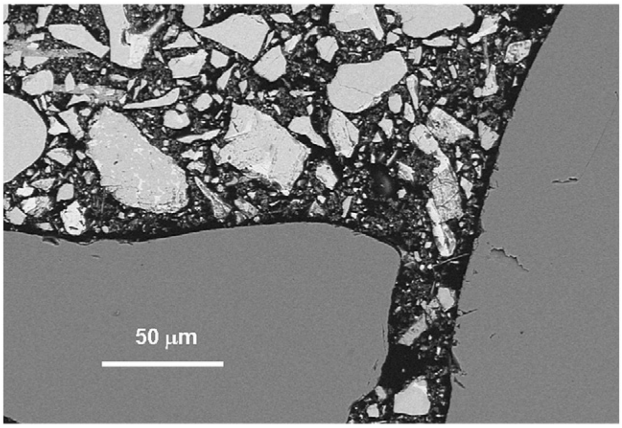

Fig. 6. SEM image from the corresponding 6-h old w/c 0.40 fast-frozen mortar.

The microstructural features exhibited in Figs. 5 and 6 are essentially identical to each other. Both images show black epoxy-filled layers adjacent to sand grains as previously observed in fast-frozen specimens prepared immediately after mixing. Indeed, the epoxy-filled black layers seen in the conventionally-dried mortar (Fig. 5) appear to be even more clearly developed than those in the corresponding fast-frozen mortar (Fig. 6).

By 6 h some hydration (especially of fine cement particle 'chips') is certainly to be expected. Both Fig. 5 and Fig. 6 show what appear to be the beginnings of a coherent structure of fine gray hydration products within the bulk of the cement paste. Such structures are absent from the black layers around the sand grains in both specimens.

Figs. 5 and 6 were selected to illustrate well-defined epoxy-filled layers free of hydration products. However, both 6-h old mortar specimens show some areas in which the originally water-filled layers had been locally invaded by precipitated calcium hydroxide. Fig. 7, taken from the fast-frozen w/c 0.40 mortar provides an example of calcium hydroxide precipitation in such spaces, as indicated by the white arrows.

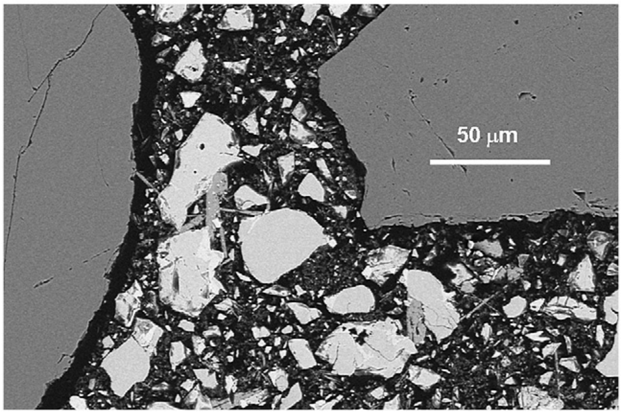

Fig. 5. SEM image of 6-h old w/c 0.40 mortar conventionally-dried at 60 °C showing black epoxy-filled layers around the sand grains.

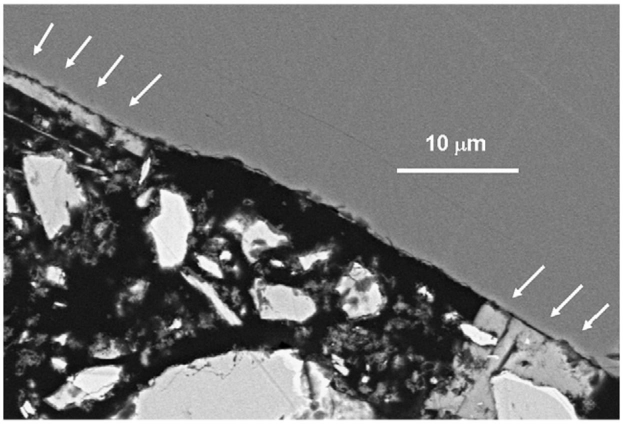

Fig. 7. White arrows point to local deposits of CH found in water-filled layer in 6-h old fast-frozen w/c 0.40 mortar.

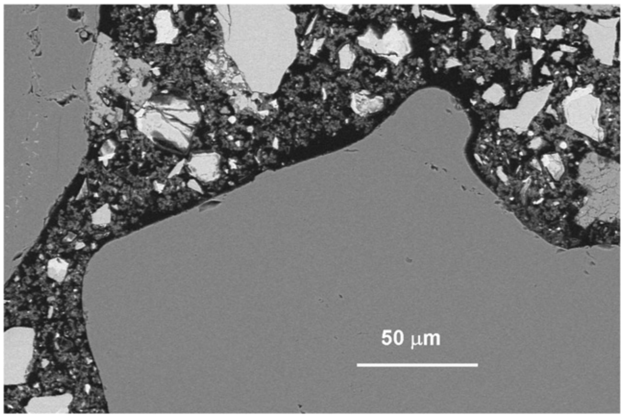

Fig. 8. Area in 12-h old conventionally-prepared w/c 0.40 mortar showing further deposition of hydration products in the water-filled layers, but the continued ability to discern their outlines in some areas.

Similar local areas containing CH precipitated within the layers are found in the corresponding conventionally-dried mortar specimen.

It appears to us that the existence of such deposits provides objective proof that the black layers illustrated in the previous images represent zones that were filled with water in the original mortars before specimen preparation, and were not induced by either method of specimen preparation.

On further hydration, as the peak rate of heat evolution is approached and passed, the tendency to deposit hydration products within the water-filled layers is greatly advanced. In our 12-h old specimens much more of the space in the water-filled layers has been filled by hydration products, and C–S–H as well as CH is now found deposited within them, as seen in Fig. 8. Nevertheless, as seen in Fig. 8, in many areas the boundary of the originally water-filled layer can continue to be discerned even at 12 h.

We have so far shown examples of the water-filled layers, which reveal a reasonably uniform thickness (typically 2–4 μm) and follow the local convolutions of the aggregate particle surface with considerable fidelity. Additionally, it is seen that wider and more irregular water-rich patches with low concentrations of cement grains occur in the fresh mortars around and between some sand grains. An example is provided in Fig. 9, taken from the w/c 0.40 fast-frozen fresh mortar that had been mixed for the extended time period.

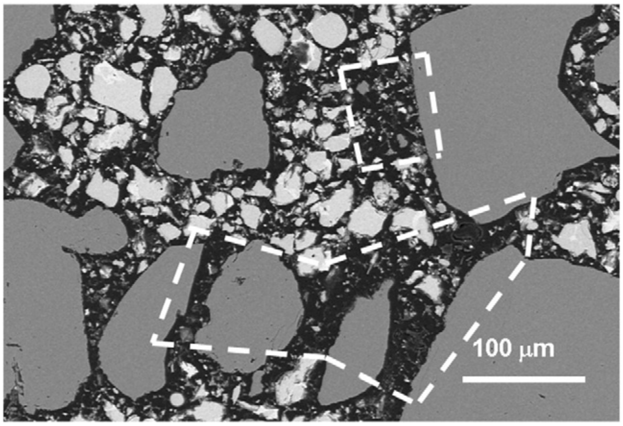

Fig. 9. Area in fast-frozen freshly-mixed 0.40 w/c ratio mortar that had been subjected to the extended mixing period. Extensive water-rich patches containing relatively few cement grains are displayed in the outlined areas.

The two areas outlined by the dashed marks in Fig. 9 depict extensive paste zones with very low concentrations of cement particles, i.e. high contents of water-filled space, in close proximity to small sand grains. Such porous patches should not be confused with the much narrower water-filled layers, examples of which can also be seen in the figure. Note also the existence of a ‘dense patch’ of closely spaced large cement grains between the two outlined porous patches extending to the upper left of the image.

3.3. Observations in specimens of mature mortars

Specimens examined at 28 days, whether conventionally-dried or fast-frozen, generally do not show recognizable water-filled layers found in the fresh and early age mortars illustrated in Figs. 1–9. It appears that such water-filled layers have been so extensively filled in by cement hydration products that their outlines can no longer be discerned.

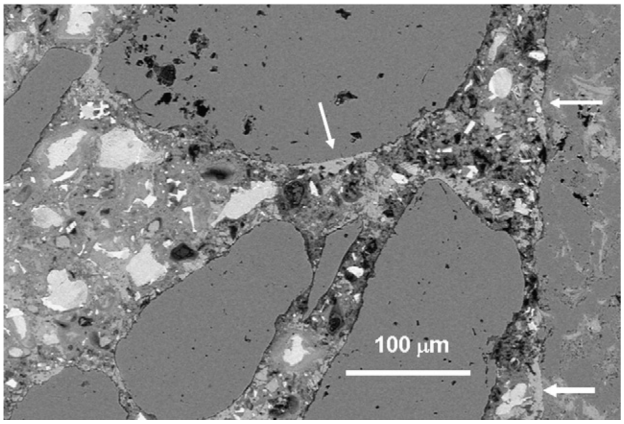

Fig. 10. Representative area in conventionally-dried 28-day old w/c 0.40 mortar specimen.

An example is provided in Fig. 10, which shows a representative area in the 28-day old conventionally-dried w/c 0.40 mortar specimen. Similar SEM images have been published many times by various authors. Note that a dense patch containing many large and only partly hydrated cement particles is visible to the left of the image and a much more porous patch containing few such particles and many appreciably-sized pores can be seen in the right-hand portion.

The image also contains examples of elongated CH deposits a few μm thick and some tens of μm long which have been deposited adjacent to sand grains; some of these are indicated by white arrows. As indicated previously, such elongated and well-oriented CH deposits along aggregate particle surfaces have been observed in mature mortar and concrete by many authors.

While the inner boundaries of most of these elongated CH deposits tend to follow the aggregate surfaces, their outer boundaries often appear irregular and convoluted, much more so than the boundaries of the water-filled layers they have invaded.

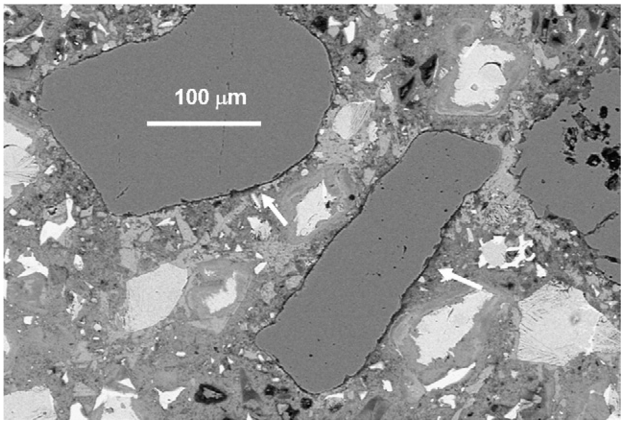

Fig. 11. Illustration of occasional separations found between sand grains and dense hardened paste in conventionally-dried 28-day old w/c 0.40 specimen.

It appears that the CH, once precipitated in the water-filled layers, often grows beyond them into connecting space within adjacent broader porous zones.

In backscatter SEM images of mature mortars, occasional narrow separations between hardened paste and sand grains may sometimes be seen. Examples are marked by white arrows in Fig. 11, from the conventionally-dried 28-day old w/c 0.40 mortar. Such occasional separations have been observed in various previous microstructural investigations, and have often been described as areas of local bond failure.

In areas of particularly dense paste, such bond failures are associated with visible shrinkage cracks. An illustration is provided in Fig. 12, taken from a 28-day old fast-frozen w/c 0.25 mortar. A number of shrinkage cracks are visible in the dense paste. In the upper left-hand area of the image, one of these cracks has turned and progressed as a bond crack between the paste and the sand grain.

These late-age bond failure cracks are typically much narrower than the water-filled layers exhibited in fresh mortars, most of them being less than 1 μm in width. It appears to us that they are most likely induced by late-age shrinkage effects, perhaps exacerbated by mechanical effects induced in specimen preparation; we do not believe that they are relics of water-filled layers.

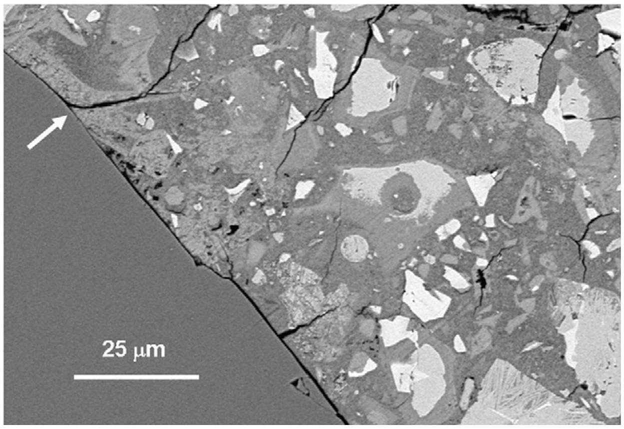

Fig. 12. Example of bond failure apparently due to shrinkage cracking, in fast-frozen 28-day old w/c 0.25 mortar specimen.

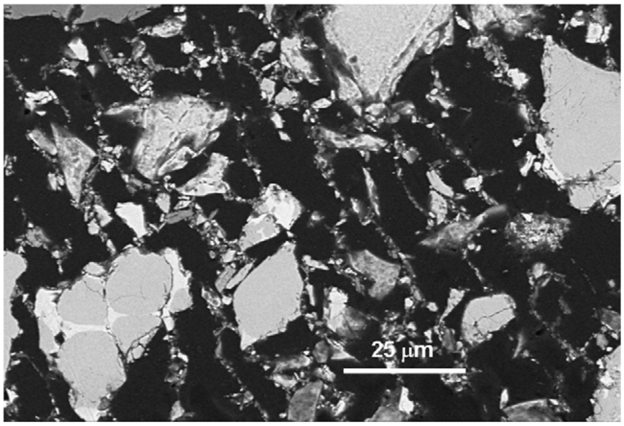

Fig. 13. Pattern of empty cells found in w/c 0.40 mortar fast-frozen immediately after mixing.

3.4. A possible ice formation feature found in several fast-frozen freshly-mixed mortar specimens

It was previously mentioned that an effect possibly attributable to ice crystal formation was found in a few of the specimens that were fast-frozen immediately after mixing. This feature, where found, is visible commonly in highly water-rich areas well away from the sand grains. An illustration is shown in Fig. 13, from a w/c 0.40 specimen fast-frozen immediately after mixing.

In the figure an elongated cellular structure can be seen consisting of black epoxy-filled spaces, bounded by narrow arrays of μm- or sub-μm sized white cement chips and similar-sized gray particles, which appear to be hydration products of the former. There is a tendency for the cells to be longer in one direction, and the long axes are preferentially aligned from lower right to upper left. Such features were found in local areas of two of the fresh mortar specimens produced by fast freezing, the w/c 0.25 and the normally-mixed w/c 0.40 specimens. They were absent in the w/c 0.40 mortar specimen that had been subjected to extended mixing, and in the w/c 0.50 specimen. They were absent in fast-frozen specimens 6 h old or older, except that a few hints of such a pattern were seen in a single 6-h old specimen (w:c 0.25), and were absent in the conventionally-dried specimens. The effect appears to represent the result of adventitious formation of fine ice crystals in areas within the cement paste that occurred in some individual fast-frozen sample preparations and not in others.

4. Discussion

4.1. Recapitulation of observations and our interpretations

Our observations and our interpretations with respect to the water-filled layers observed in fresh mortars can be summarized as follows:

1. The water-filled layers depicted in this paper are *not* artifacts of the fast freezing specimen preparation procedure, since they are found equally in the corresponding conventionally-dried specimens.

2. These water-filled layers are found adjacent to most, but not all, of the sand grains in the fresh and early age mortars. They may or may not extend completely around the sand grains on which they are found. While specimen orientation with respect to gravity was not monitored, no bias toward a particular orientation was recognized within the SEM images.
3. The water-filled layers can be quite uniform in thickness and tend to follow the local sand grain perimeter quite closely. Their thickness, generally between 2 and 4 μm, represents several thousand monomolecular layers of water.
4. The "water" in these layers must necessarily not be water per se, but rather the high ionic strength mix solution produced when cement and water are mixed. Such solutions quickly become saturated or supersaturated with respect to calcium hydroxide.
5. These water-filled layers in *fresh* concrete appear to be associated with the common occurrence in *hardened* concretes of oriented layers of calcium hydroxide of roughly the same thickness along aggregate surfaces.
6. Since these layers may be in contact with adjacent porous patches, the calcium hydroxide deposits nucleating within them are not necessarily confined to the layers per se, but may extend into adjacent porous spaces as well.
7. In mature mortars and concretes, the narrow "bond separations" occasionally found between the paste and the aggregate appear to have a different origin, and do not appear to be relics of the water-filled layers.

4.2. Possible explanations for the existence of water-filled layers

The existence and appearances of water-filled layers have heretofore been described without any particular explanation for them having been attempted. Several possibilities are considered below.

The well-known "wall effect" immediately comes to mind. The wall effect has been described by many authors, and has been recently summarized (and illustrated) by Scrivener et al. [13]. These authors indicated that since aggregates are usually several orders of magnitude larger than cement grains, the presence of aggregates disrupts the normal packing of the cement grains in fresh concretes, with the result that "a zone closest to the aggregate contains predominantly small grains and has a significantly higher porosity, while larger grains are found further out". The wall effect so described is quite different in character from occurrence of sharply-defined water-filled layers reported here, which seem to be completely free of *all* cement grains, large or small.

The possibility that such layers might represent bleeding pockets trapped under sand grains has been considered but is somewhat suspect, since the layers occur around sand grains with no apparent orientational bias. Also, bleeding is a time-dependent process and its effects would not be fully evident immediately after mixing. Furthermore, as shown in Fig. 1, the water-filled layers were found to be well developed in low w/c mortars, where no bleeding would be expected.

Some years ago de Rooij et al. [14–16] called attention to the phenomenon of "syneresis" occurring in cement pastes. These authors observed by optical microscopy that thin pats of freshly-mixed cement pastes placed in optically-transparent cells shrank spontaneously toward their centers, exuding a narrow zone of clear solution around their perimeters. Such a process of spontaneous paste contraction might conceivably take place in mortars as well as in pastes, causing the paste to shrink away from the sand grains and leave water-filled layers adjacent to them. However, the syneresis observed by de Rooij and colleagues appears to be time-dependent and relatively slow, in contrast to the effect found here almost immediately after mixing.

It is obvious that further investigation of the origin of these layers is needed.

4.3. Implications with respect to the interfacial transition zone

It has been established by careful measurements carried out by a number of authors [17–20] that in hardened conventional concrete there is a relationship between the *averaged* content of measurable pores in the cement paste and distance to the nearest aggregate interface, within a zone generally designated as the interfacial transition zone (ITZ). There is general agreement that the overall width of the affected ITZ zone is of the order of 30 to 50 μm, i.e. about 10 times the width of the water-free layers illustrated here. Within this zone the averaged porosity increases progressively, and the average residual cement content decreases progressively as the actual interface is approached. Both effects in hardened concrete are conventionally attributed to the wall effect in the fresh concrete as discussed previously.

These averaged effects tend to mask a great deal of local variation including the effects of local dense and porous patches within the cement paste. Porous patches occur within the conventional ITZ, and often adjacent to some aggregates, as shown in Fig. 9 of the present paper, and as was illustrated for hardened concretes by Diamond [21]. Thus the relationship, if any, between the narrow but sharply-defined water-filled layers found in fresh mortars, and the much broader ITZ zones in hardened concrete is not immediately apparent.

4.4. Implications with respect to cement hydration models

Finally, it appears that the temporary existence of water-filled layers in fresh and early age systems provides yet another complication for those attempting to realistically model the processes of cement hydration as they occur in mortars and concretes.

5. Conclusions

Examinations of the microstructural arrangements in fresh mortars reveal the existence of layers of water-filled spaces of the order of 2–4 μm wide adjacent to many or most sand grain surfaces. The mortars in question encompassed w/c ratios ranging from 0.50 to 0.25; the heavy dose of superplasticizer, necessary to obtain fluidity for the w/c 0.25 mortar did not appear to influence these findings. The existence of the water-filled layers is not an artifact of the fast freezing and epoxy impregnation specimen preparation procedures used, since they are found with conventionally-dried specimens as well. These layers are initially free of both cement grains and cement hydration products, but after a few hours occasional isolated calcium hydroxide crystals are precipitated within them, followed subsequently by C–S–H deposits. The boundaries of these water-filled spaces often follow the local convolutions of the aggregate surface with considerable fidelity. In some places the outline of the originally water-filled layer can be recognized for at least 12 h, but recognizable relics of such spaces were not generally found in mature (28-day old) mortars.

Previous indications that the 'patchy' microstructures found in hardened mortars and concrete are inherited from the fresh state were confirmed.

Acknowledgment

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