Investigations Into the Microstructure of Fresh Portland Cement Mortar

K. O. Kjellsen[1], S. Diamond[2]
[1]*Norcem AS, Brevik, Norway;* [2]*Purdue University, West Lafayette, U.S.A.*

ABSTRACT

Specimens for backscatter SEM examination were prepared from freshly-mixed mortars, and from the same mortars hydrated for 6 hours, 12 hours, and 28 days. Small samples were fast-frozen in liquid nitrogen, sublimed at low temperature, and epoxy impregnated and polished. Reference specimens were also prepared from the same mixes at 6 hours and later, using conventional 60^{o}C drying. Comparison of the freeze-dried and conventionally-dried specimens at 6 hours and beyond showed identical microstructural features. In the fresh state; the larger cement grains were found to be distributed inhomogeneously, 'pockets' of paste being either relatively densely packed with large cement grains, or largely bereft of such grains. These pockets gave rise to densely packed patches and porous patches in the mature hardened mortars. Layers of water on the order of 5 μm thick seemed to have been present around some of the sand grain surfaces in the fresh and very early age mortars. By 6 hours isolated crystals of $Ca(OH)_2$ were deposited within these layers; subsequently they were filled in with more $Ca(OH)_2$ and deposits of C-S-H. Several other features seen in fresh and very early-age mortars are briefly described.

1. Introduction

The microstructures of Portland cement pastes in set and hardened mortars and concretes have been extensively investigated in recent years, primarily by backscatter-mode scanning electron microscopy (SEM). Comparatively little investigation has been reported on the corresponding microstructures of fresh concretes, although many of the features present in the hardened systems stem from original spatial arrangements of cement grains within the assemblage of sand (and coarse aggregate) grains in the fresh condition.

Microstructural studies of fresh mortars can provide much of the needed information, without the complexity induced by coarse aggregates. However, most studies have been on fresh cement paste rather than fresh mortars.

The experimental difficulties in such studies are obvious. Means must be found to prepare specimens of the quasi-fluid system without seriou sly distorting the grain-to-grain arrangements pre-existing in the material.

Escadeillas and Maso [1] attempted to quickly freeze-dry fresh pastes and mortars by immersing them in liquid nitrogen, but used large samples contained in 20 mm-diameter plastic tubes. Their freezing procedure almost certainly induced ice crystallization. Uchikawa et al. [2] confined their examinations to pastes rather than mortars; they used small samples (ca. 0.5 g) quickly frozen on a metal plate pre-cooled to liquid nitrogen temperature before immersion in the liquid nitrogen. Sublimation and backscatter SEM observations were carried out in a cryogenic SEM microscope chamber, maintained at -120^{o}C. Very recently a somewhat similar technique was applied to imaging fresh cement pastes by Zingg et al. [3], except that that they employed a high-pressure freezing technique, developed for the study of biological tissues. A very different technique was employed by Holzer et al. [4], who examined the structure of the residue retained by filtering fresh cement paste to remove the pore solution for analysis; these authors used backscatter imaging in an ESEM after drying the paste residue at 100^{o}C and then impregnating with epoxy resin and polishing. Clearly the grain-to-grain arrangements would not have been preserved in such specimen preparation.

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. 15,000x. Such studies suggest that even with very fast freezing under high pressure, it is difficult to completely avoid the generation of extremely fine ice crystals [5]. Such crystals have been shown to pierce the tissues and disrupt the fine internal details of the tissue structures [6]. However, very fine ice crystals would not necessarily influence the grain-to-grain arrangements of cement and sand grains in fresh mortars; these being so much larger and more massive than the biological tissue features. Nevertheless the possibility of alteration of the grain-to-grain arrangements and alterations in the details of the developing early hydration products must always be considered in examinations of even extremely rapidly frozen systems.

In the present paper we report the results of examinations of fresh and early hydration stage mortars. Very small samples were fast-frozen in liquid nitrogen, sublimed at low temperature, then epoxy impregnated, hardened, and polished to produce backscatter SEM specimens. Specimens were prepared immediately after mixing, and subsequently after 6 hours, 12 hours, and 28 days. For comparison with the freeze-dried specimens, 'control' specimens were prepared by conventional drying at 60^{o}C, followed by the same epoxy impregnation and polishing procedures for mortars hydrated for six hours and beyond; conventional drying immediately after mixing would induce obvious shrinkage effects and so such specimens were not prepared.

2. Experimental

2.1 Materials, mixing, and curing

The mortars were mixed according to the European Standard EN 196-1 (Methods of Testing Cement. Part 1: Determination of Strength). Compositions are provided in Table 1. The mixes were prepared at w:c ratios of 0.25 and 0.40 as well at the 0.50 w:c ratio specified in the Standard.

In these mortar mixes the paste volume was kept constant at 42%, thus giving a constant sand volume of 58%. One bag (1350 g) of the siliceous reference CEN sand (cf. EN 196-1) was used for each mix batch. The cement used was a Swedish low-alkali sulfate-resistant cement (equivalent to ASTM Type V). The cement 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 compositional data indicate that the cement was of very low alkali content and contained almost no C_3A, the calculated Bogue composition being 57% C_3S, 21% C_2S, 0.8% C_3A, and 14% C_4AF. The Blaine specific surface area and density were respectively 309 m^2/kg and 3220 kg/m^3.

Batch compositions for all three mixes are given in Table 1.

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*	163	205	225
Superplasticizer	22.8	3	-

*Total water, including water in plasticizer

In order to obtain workable mortars at the two lower water:cement ratios it was necessary to incorporate a superplasticizer. As indicated in Table 1, a modest dose of sulfonated naphthalene superplasticizer (Mighty 150); was employed with the w:c 0.40 w:c ratio mix, and a heavy dose was needed for the w:c 0.25 mix.

After mixing the mortars were placed in molds and conditioned as prescribed by the specified Standard Method. Curing took place at 100% RH and room temperature, approximately 20°C.

2.2 Specimen Preparation

Specimens were freeze-dried immediately after mixing, and also after 6 hours, 12 hours, and 28 days. In each case ca 0.25 g portions of mortar were sampled from the mix and quenched in liquid nitrogen. The frozen samples were then subjected to low-pressure, low-temperature sublimation (at pressures between ca. 10^{-4} and 10^{-2} Mbars) over a period of three days. According to the ice - water vapor phase boundary in the water phase

diagram, these pressures correspond to maintaining temperatures between ca -90°C and ca -60°C during the sublimations. Such temperatures would restrict (but probably not completely prevent) the Ostwald growth of some of the ice nuclei that were probably produced during the freezing step. As indicated previously, comparison specimens were prepared from the w:c 0.40 mixes (at 6 hours and beyond) using conventional drying at 60°C in order to check for possible effects of such ice crystal growth.

The degree of removal of water during this extended sublimation was checked against oven drying, and water removal was found to be complete.

The handling of the fragile freeze-dried specimens, the epoxy impregnation procedure, and the polishing procedures used were as described previously [7,8]. Parallel observations in backscattered and secondary electron modes indicated that the as-prepared specimens were flat and fully impregnated.

The specimens were then carbon coated and examined in backscatter in a Hitachi model S-4300 Field-Emission SEM, with the accelerating voltage kept at 10 keV throughout. A number of areas of each specimen were examined to be certain that the images presented are representative. In all, approximately 320 backscatter SEM images were produced in this study.

3. Results

3.1 Comparison of freeze-dried and conventionally-dried SEM images

In Fig. 1 we compare representative fields taken at 1,000x, of freeze-dried and 60°C-dried w:c 0.40 mortars at six hours. The features exhibited in the two images appear to be identical for all practical purposes. Effects that might be produced by ice crystals growing between the cement grains would presumably be quite different in character from effects that might be induced by the conventional drying treatment. Thus the fact that identical microstructures are observed for the two different modes of specimen preparation seems to be evidence that the freezing and sublimation processes have not induced any special artifacts that are visible at these magnifications. Similar comparisons for microstructures at later ages confirm these findings.

In Fig.1 and most subsequent images the sand grains are generally a uniform gray, the unhydrated cement grains are bright, the fine-textured cement hydration products are dark gray, and the epoxy-filled (originally water-filled) spaces are black. Discussion of the actual features found in Figure 1 is postponed until after discussion of additional images that display similar features.

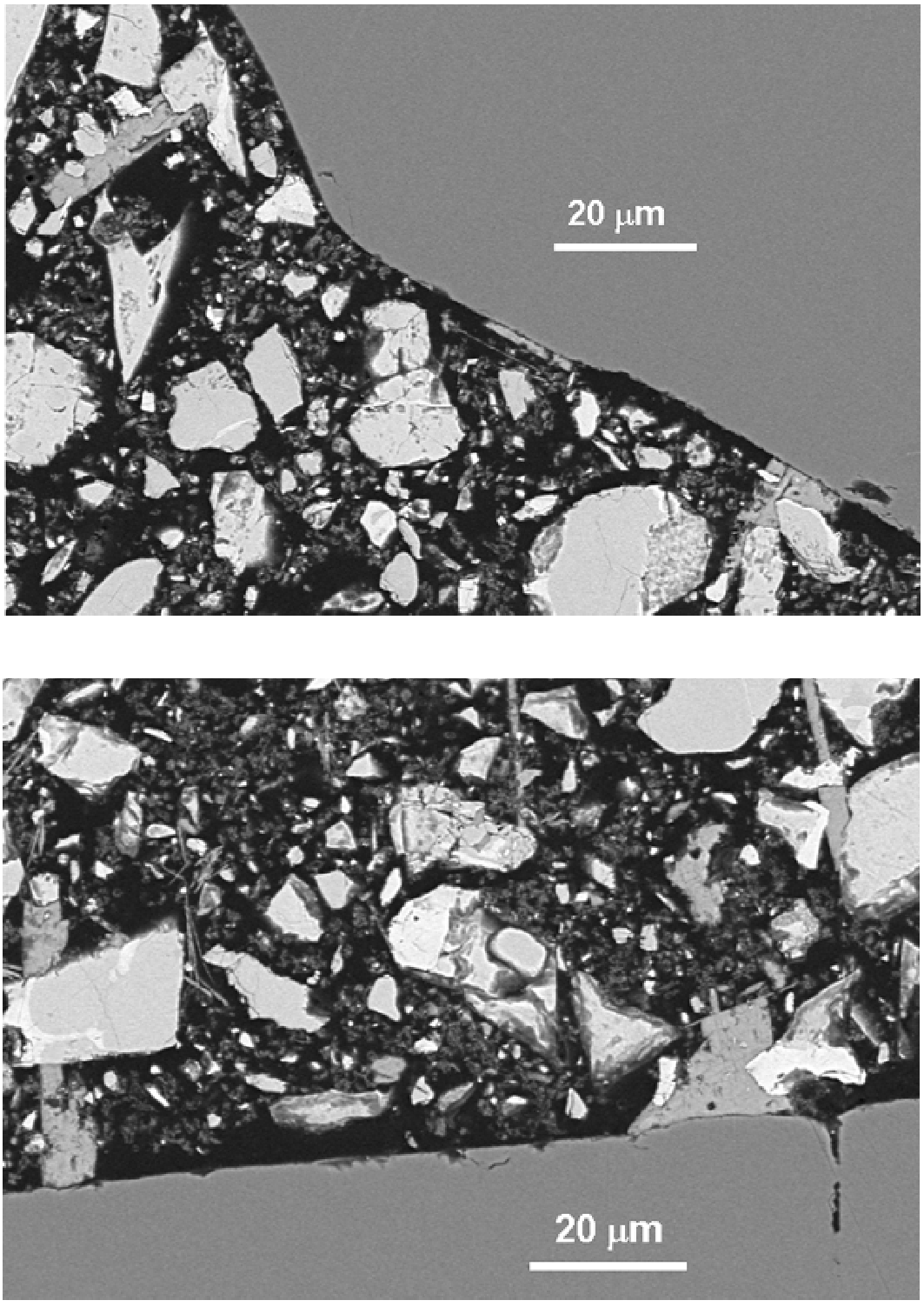

Fig. 1. Comparison of w:c 0.40 mortars at 6 hours: above, after freeze-drying; below: after conventional drying at 60^{o}C.

3.2 Patchy structure of the mortar

Figure 2 provides a low magnification view of a representative area in the 6 hour-old freeze-dried w:c 0.50 mortar. While some degree of setting was attained by this time, the hardened mortars showed very little evidence of cement hydration. The mortar at this stage was extremely soft and weak, and the specimens were plucked out of the mass with light finger pressure.

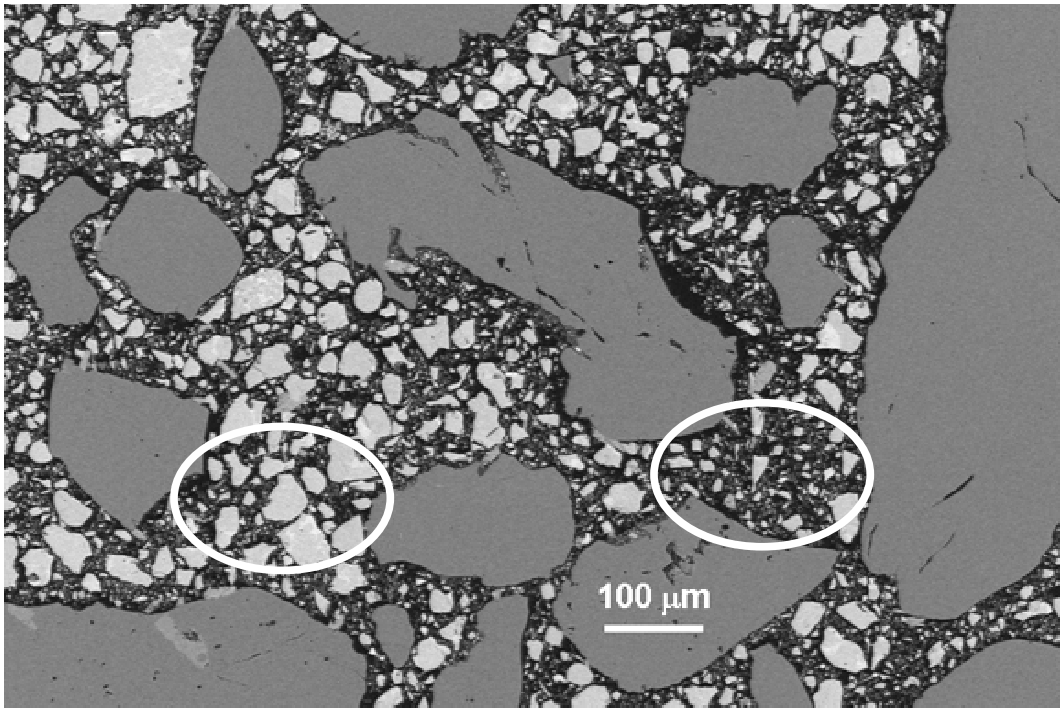

Fig. 2. Low magnification image of 6 hour old w:c 0.50 mortar.

The inhomogeneous spatial distribution of the larger cement grains is evident. Closely-spaced aggregations of large cement grains are seen in the outlined oval area to the left; in contrast, the outlined oval area to the right contains only a single cement grain of comparable size. Dense packing of large grains is found even in some of the narrower paste areas between adjacent sand grains.

Fig. 3 is a higher magnification image taken to show further details of the assemblage of cement grains within the general area of the right oval of Fig. 2. The bright white cement grains seen here (with few exceptions) are less than 20 μm in size; indeed, most are substantially smaller than this. These small grains appear to be quite widely separated from each other, and the local water:cement ratio seems to be very high.

In contrast, Fig. 4 is a local area in the specimen where much larger cement grains predominate, and many are quite closely spaced.

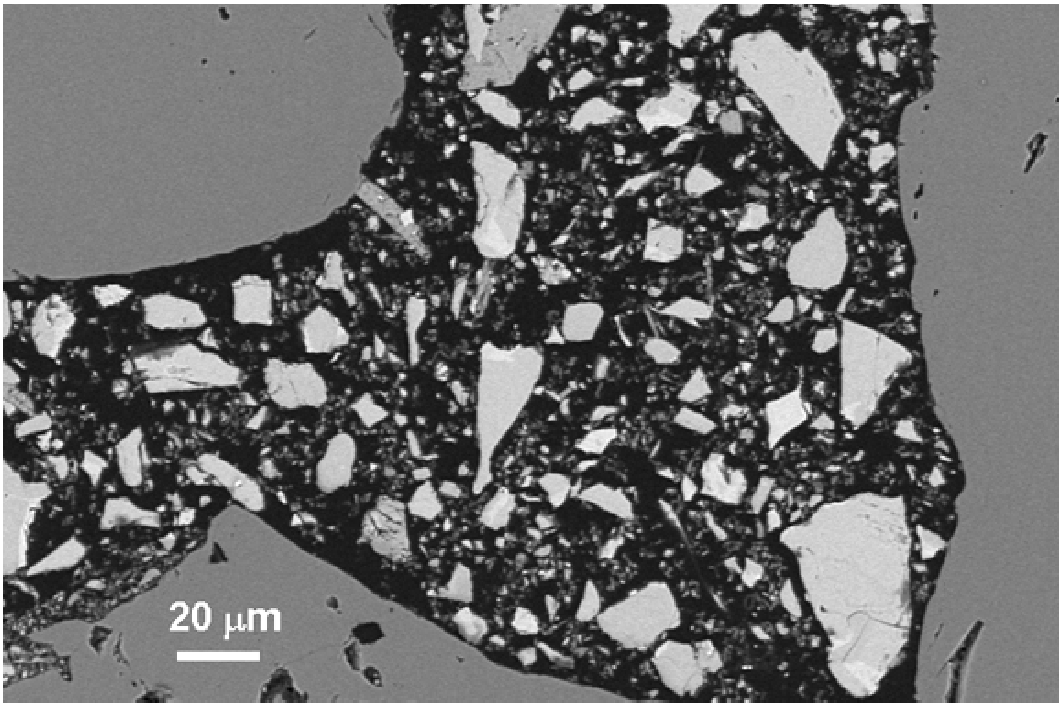

Fig. 3. A higher-magnification view of an area around the oval in the right-hand part of Fig. 2 showing a lack of large cement grains.

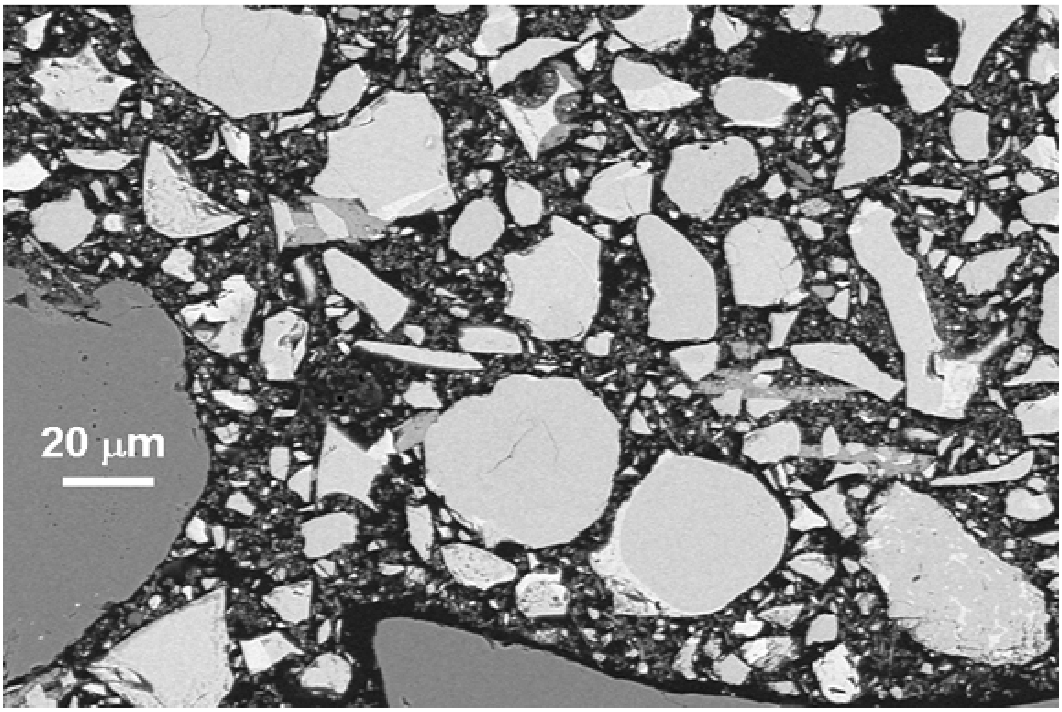

Fig. 4. A higher-magnification view of an area in the left part of Fig. 2 showing a predominance of larger cement grains, in contrast to Fig. 3.

It is clear from Fig. 5 that this patchy structure seen in the hardly-hydrated mortar at six hours is inherited from the as-mixed mortar. Fig. 5 was taken from the freeze-dried specimen prepared immediately after mixing.

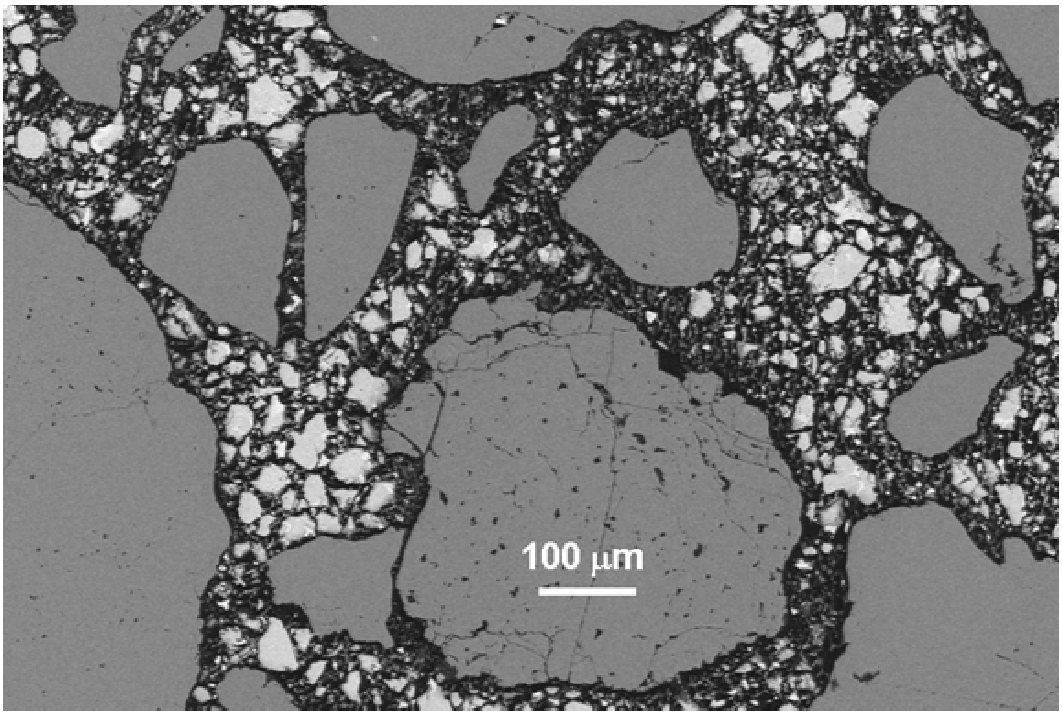

Fig. 5. Low-magnification view of w:c 0.40 mortar specimen prepared immediately after mixing.

This local variation in content of large cement grains in the fresh (or hardly hydrated) mortar leads to corresponding variations in the later-stage hardened mortar. In particular, the local degree of hydration and the local content of residual pores are much affected, leading to a "patchy" microstructure in the mature mortar. This patchy structure has been documented by backscatter SEM in hardened mortars and concretes [9-10], and recently by micro-CT [11]. Fig. 6, taken from the w:c 0.50 mortar hydrated for 28 days, well illustrates this effect.

The existence of dense and porous patches in the mature mortar was also observed in the w:c 0.40 mortars, but not in the w:c 0.25 mortars. As shown in Fig. 7, in the mature w:c 0.25 mortars essentially the entire paste exhibits completely dense microstructure. It can be seen that the appearance of the dense patch area to the right of Fig. 6 (w:c ratio 0.50) quite resembles the appearance of the fully dense paste microstructure of Fig. 7 (w:c ratio 0.25).

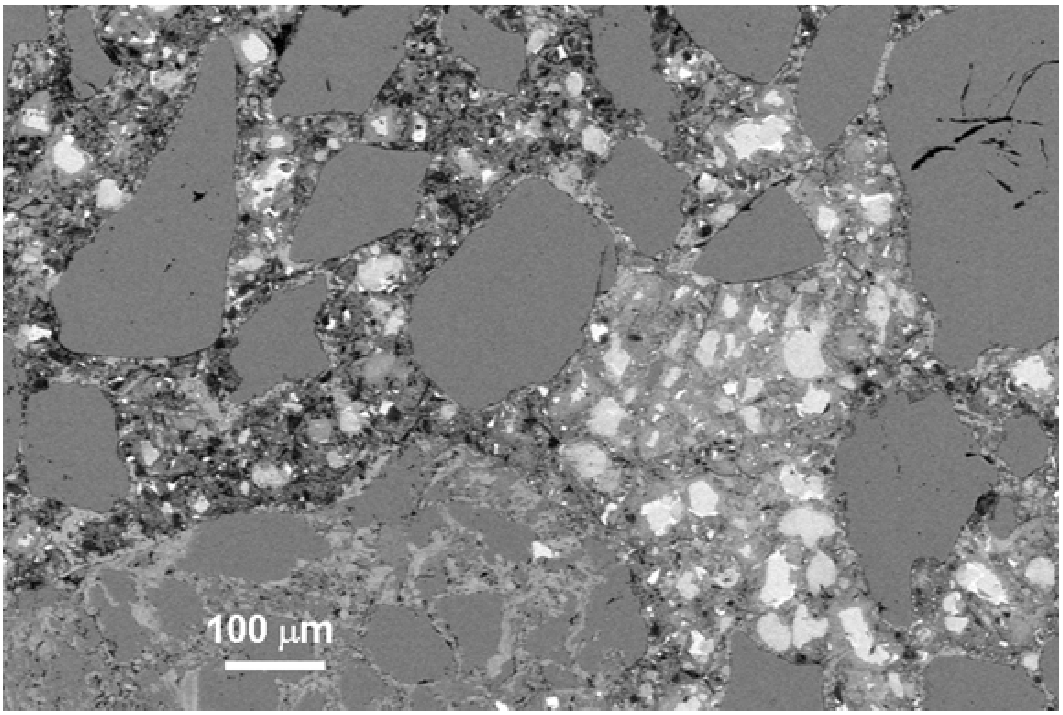

Fig. 6. Low-magnification view of w:c 0.50 mortar hydrated for 28 days, showing the 'classical' patchy structure: a porous paste area with almost no residual cement grains on the left and a dense paste area heavily populated with large residual cement grains on the right.

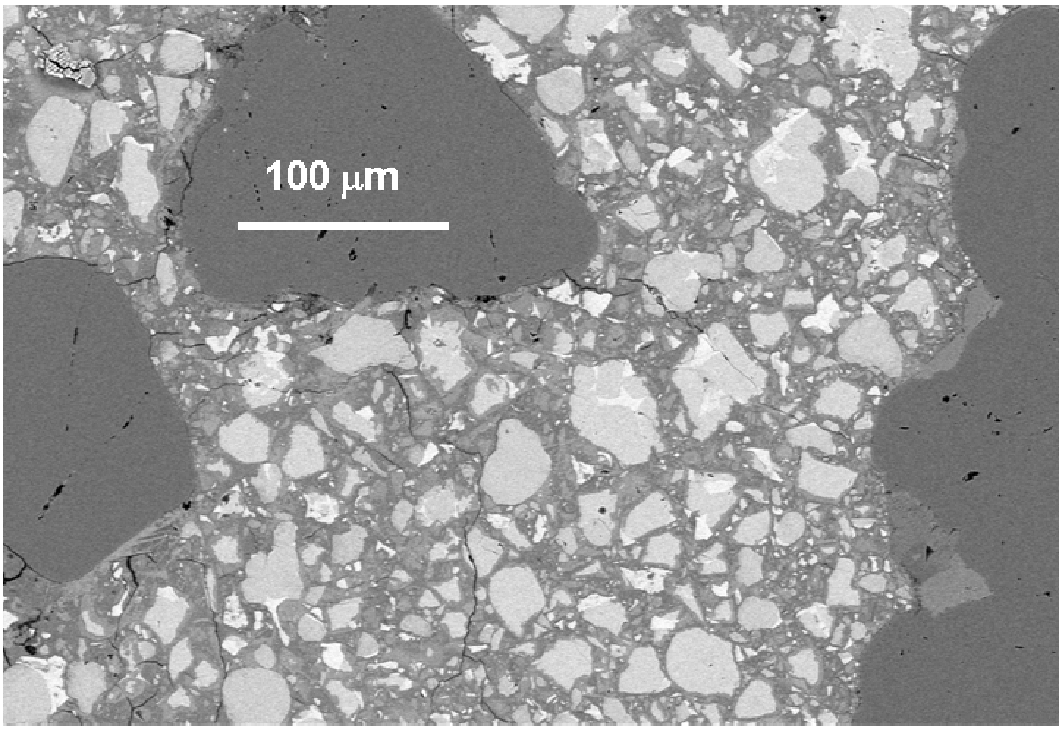

Fig. 7. Characteristic fully-dense microstructure of w:c 0.25 mortar at 28 days.

3.3 Additional Observations

A number of additional observations have been recorded, which will be described in more detail elsewhere.

3.31 Apparently water-filled layers adjacent to sand grains

In the SEM examinations of the fresh mortars and those examined at 6 hours of hydration, it was observed that some of the areas adjacent to surfaces of the sand grains are filled with epoxy, and are seen to be locally almost free of cement grains or hydration products. These areas vary in thickness but are of the order of 5 μm thick in many places. In some, but not all, areas their boundaries are remarkably sharp.

Such areas appear in the 60°C-dried 6-hour old mortars as well as in the corresponding freeze-dried mortars; thus it seems evident that they do not represent an unusual effect induced by freeze drying.

Such open areas are visible around most of the sand grains in the freshly-mixed freeze dried mortar of Fig. 5, and can be seen at higher magnification around parts of the sand grains in Figs. 3 and 4. In both the upper and lower images of Fig. 1 (both at 6 hours of hydration) isolated crystals of $Ca(OH)_2$ are found to have precipitated within the otherwise seemingly water-filled spaces. Two such crystals are present in the space below the large sand grain that occupies the upper right portion of the upper image of Fig. 1 (from a freeze-dried specimen). Two larger ones appear in the space immediately above the large sand grain in the lower image of Fig. 1 (from a conventionally-dried specimen). The presence of these $Ca(OH)_2$ crystals within the apparently water-filled space suggests that it is not empty space produced by shrinkage of the paste away from the sand grain on either freeze-drying or conventional drying, and later intruded by epoxy resin. This possibility does exist, however.

These spaces are less definite as hydration proceeds. By 12 hours they appear to be invaded by C-S-H gel precipitating from solution, as well as by additional $Ca(OH)_2$ crystals. By 28 days the mortars show little evidence of these original empty areas, even in the porous patches.

3.32 Near-interface microstructure

In these mortars the “near interface” zones, i.e. the zones of cement paste adjacent to the sand grains, were seen to be quite variable from place to place. The microstructural features of the fresh and very early-age hardened paste “inward” of the actual interface (or inward of the seemingly water-filled areas) are extremely variable. In some fields smaller cement grains

concentrate preferentially toward the sand grain surfaces; in other fields large cement grains are densely packed close to the sand grains. The conventional notion that a uniform gradient of cement grain packing extends inward from all aggregate surfaces exists so as to produce a corresponding uniform gradient of porosity, i.e. a conventional "interfacial transition zone", is far from what is seen. Instead, this variable packing of cement grains near sand grains in different areas results in a correspondingly variable near-interface microstructure in the hardened state.

4. Discussion

The inhomogeneous spatial distribution of large cement grains in fresh mortars and concretes - leading to the later development of dense and porous patches after hydration takes place - was postulated originally by Idorn [12] to explain his observations of dense and porous areas in mature field concretes.

5. Conclusions

1. The method of freezing and low-temperature sublimation employed here results in the production of polished mortar specimens that show microstructures seemingly identical to conventionally-prepared backscatter SEM specimens when compared for mortars 6 hours old and older. Freeze-dried specimens that were prepared immediately after mixing show similar features, but were not directly compared with conventionally dried specimens.

2. Both conventionally-dried and freeze-dried mortar specimens show only little evidence of hydration at 6 hours, but both clearly exhibit inhomogeneous spatial distributions of large cement grains. Similar inhomogeneous distributions of large cement grains were seen in freeze-dried specimens of fresh mortars prepared immediately after mixing.

3. These local irregularities in packing of cement grains in the fresh and very-early age nearly unhydrated mortars give rise to dense and porous patches in the fully hardened state, at least for w:c 0.40 and w:c 0.50 mortars. In contrast, hardened w:c 0.25 mortars develop an entirely dense paste microstructure, within which many of the larger cement grains remain almost unhydrated.

4. In the earliest hydration stages empty areas of the order of 5 μm (or sometimes larger) in thickness were seen adjacent to many sand grain surfaces. At 6 hours isolated calcium hydroxide crystals are clearly seen to exist in such areas, suggesting that they are presumably water-filled spaces rather than empty spaces created by drying shrinkage. Subsequently, deposits of C-S-H and additional $Ca(OH)_2$ seem to progressively fill in these areas, and they are not seen at 28 days.

REFERENCES

[1] G.C. Escadeillas, J.C. Maso, Approach of the initial state in cement paste, mortar, and concrete, in S. Mindess (Ed) Ceramic Transactions. Vol 16, Advances in Cementitious Materials, American Ceramic Society, Westerfield, Ohio, 1991, pp.169-184.

[2] H. Uchikawa, S. Uchida, S. Hanehara, Flocculation structure of fresh cement paste determined by sample freezing-backscattered electron imaging method. Il Cemento1 (1987) 3-22.

[3] A. Zingg, P. Gasser, F. Winnefeld, A Kaech, J. Pakusch, S. Becker, L. Holzer, Cryo-microscopy for fresh cement pastes: First results, Paper presented at the Eighth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Sorrento, Italy (2006).

[4] L. Holzer, F. Winnefeld, B. Lothenbach, D. Zampini, The early-cement hydration: a multi-method approach, in G. Grieve and G. Owens (Eds.) Proc. 11th ICCC, Durban, South Africa (2003) pp. 236-248.

[5] J. Dubochet, High pressure freezing for cryoelectron microscopy, Trends in Cell Biology 5(9) (1995) 366-368.

[6] K.G. Schwabe, L.Terracio, Ultrastructural and thermocouple evaluation of rapid freezing techniques, Cryobiology 17 (1980) 571-584.

[7] K.O. Kjellsen, A. Monsøy, K. Isachsen, R.J. Detwiler, Preparation of flat-polished specimens for SEM-backscattered electron imaging and X-ray microanalysis – Importance of epoxy impregnation, Cem Concr Res 33 (2003) 611-616.

[8] K.O. Kjellsen, B. Lagerblad, Microstructure of tricalciumsilicate and Portland cement systems at middle periods of hydration – development of Hadley grains, Cem Concr Res (2006) (accepted for publication).

[9] S. Diamond, Percolation due to overlapping ITZs in laboratory mortars? A microstructural evaluation, Cem Conc Res 33 (7) (2003) 949-955.

[10] S. Diamond, The patchy structure of cement paste in conventional concretes, in K. Kovler, J. Marchand, S. Mindess, J. Weiss (Eds.) Concrete Science and Engineering: A Tribute to Arnon Bentur, RILEM Proc. PRO 36, RILEM Publications S.A.R.L, Paris (2004) pp 85-94. .

[11] S. Diamond, E. Landis, Microstructural features of a mortar as seen by computed microtomography, Materials and Structures (2006), in press.

[12] G.M. Idorn, Marine concrete technology, J Coastal Res 7 (4) (1991)1043-1056.