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Review article

On the occurrence of hollow-shell hydration grains in hydrated cement paste

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Abstract

In this paper, we provide the original illustrations of the formation and morphological characteristics of hollow-shell hydration grains taken from the 1972 thesis of the first author, along with more recent illustrations of the occurrence and importance of this feature as a normal mode of hydration of certain cement particles.

Keywords: Cement paste; Microstructure; Hydration; SEM; Pore size distribution

1. Introduction

The present paper represents an effort by the third author to provide an appropriate record in the literature of the original investigations carried out by D.W. Hadley in which hollow-shell hydration grains were first shown to occur as characteristic features of hydrated cement paste, and also to provide some more recent context. The original investigations referred to were carried out by Hadley during the period from 1969 to 1972 under the supervision of W.L. Dolch and with technical assistance provided by the third author. The results were reported in Hadley's Ph.D. thesis at Purdue University [1], which has been widely quoted but not widely disseminated. Dr. Hadley passed away in 1987 and Professor Dolch is recently deceased. In a sense the present paper is intended as a memorial to both of them.

2. Materials and methods of investigation

The primary focus of Hadley's investigation was the nature of the cement-aggregate bond, rather than hollow-shell hydration grains. Accordingly, the specimens and procedures he used were designed to study interfacial areas rather than "bulk" cement paste.

Most of the specimens he studied were prepared by casting a pat of neat cement paste, roughly one half inch in diameter, on the flat surface of an aggregate (or glass slide) substrate. The pastes were prepared from an ASTM Type I cement of normal composition. Its Bogue calculated contents of C_3S, C_2S, C_3A, and C_4AF were, respectively, 51.2, 23.8, 11.0, and 6.0%; the SO_3 content was 2.4% and the total alkali content was 0.38% equivalent Na_2O.

Pastes were mixed at 0.50 and 0.25 water:cement ratios, the former by hand mixing, the latter by shaking in a specially adapted paint mixer for 5 min. The substrates included standard glass petrographic microscopy slides, a pure calcitic white marble, and a well-cemented quartzite. The pastes of 0.50 water:cement ratio were simply cast against the cleaned substrate surfaces; the 0.25 water:cement ratio pastes were applied to the substrate and then subjected to vibration to consolidate them appropriately.

Immediately after preparation the substrate-paste specimens were placed over water in Petri dishes, and the dishes were sealed and stored for 8 h. The specimens were then further cured under saturated limewater solutions for periods of up to 28 days.

Hadley developed a procedure for exposing the surface of the paste in contact with the glass slide substrate by drying the specimens over magnesium perchlorate. It was found that the shrinkage stresses produced caused an almost complete separation of the paste from the substrate, and the two could be separated by simply tapping the specimen. He then went on to measure the extent of orientation of $Ca(OH)_2$ with depth into the paste by removing successive layers of material and carrying out X-ray diffraction measurements of orientation at each freshly exposed layer. This procedure

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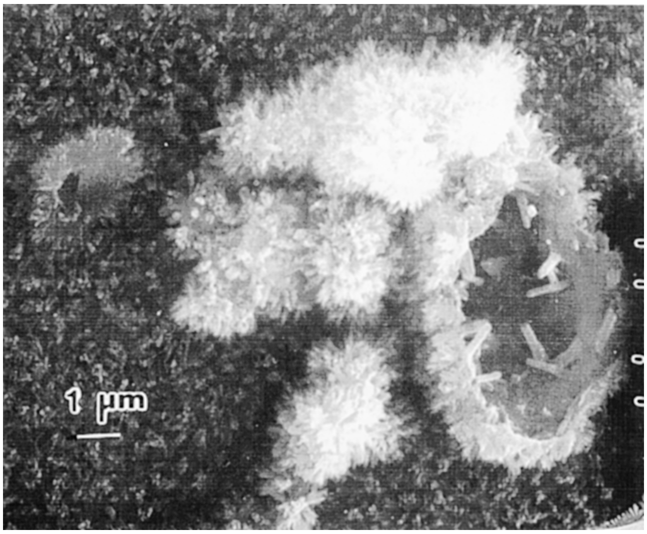

Fig. 1. Ruptured hollow-shell hydration grain on duplex film attached to glass slide of 1-day-old 0.5 water:cement specimen after separation from bulk paste by drying over magnesium perchlorate.

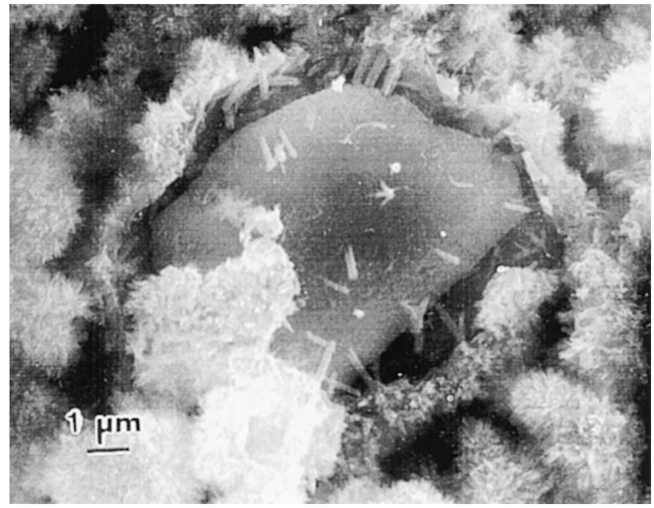

Fig. 2. Large ruptured grain with most of its core not dissolved. Glass slide and attached material from 1-day-old 0.5 water:cement specimen.

was later adapted by Grandet and Ollivier [2] and was used by them to estimate the thickness of the interfacial zone.

Hadley also carried out secondary mode scanning electron microscope (SEM) investigations of the paste surface (previously in contact with the substrate) and the corresponding substrate surface using a Jeol SMU-3 equipped with a Nuclear Diode Model 707 energy-dispersive X-ray analysis system.

3. Occurrence of hollow-shell grains at cement paste-substrate contacts

Hadley observed that for young samples a thin “duplex film” of calcium hydroxide and C-S-H gel remained on the surface of the substrate after its separation from the cement paste. In specimens examined as early as 1 day, he found a number of hydrated cement grains clinging to this duplex film on the substrate side: grains that before separation had been in contact with both the substrate “above” and the bulk paste “below.” The hydrated cement skin of some of these hydrated grains had been ruptured during the separation, revealing their interiors.

Many of these hydrated cement grains were hollow, as shown in Fig. 1, which shows a ruptured grain about 7 μm long. Rod-shaped particles, presumably ettringite, are seen to project into the empty space inside the shell to a distance of approximately 1 μm, suggesting that if the shell was not originally entirely hollow, a gap of at least this size had existed between the shell and the unhydrated cement core.

Illustrations of an incompletely hollowed-out shell with a residual core and a gap separating it from the surface shell material are provided in Figs. 2 and 3. Hadley provided a number of such figures for 1-day old specimens. His description of one of them is as follows:

> This [figure] shows a grain in which the hydration shell has been partly pulled away during separation [of the substrate from the paste] exposing the interior structure. Note that the remnant grain has been largely rounded by solution, and that it is significantly smaller than the cavity in which it rests. Notice also that the remnant grain is joined to the surrounding hydration product [shell] by several acicular crystals. The presence of these acicular crystals is helpful in indicating the void space within a hydration shell when the remnant grain has pulled away. In all instances observed, a considerable void has been found between the remnant grains and their jackets of hydration product.

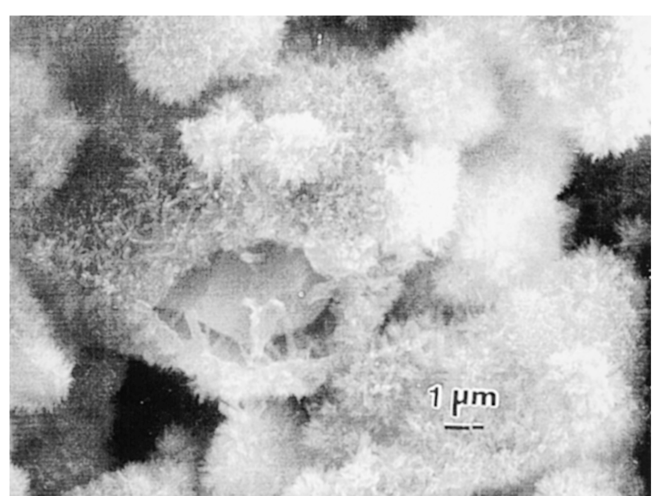

Fig. 3. Grain showing only small visible area where shell is ruptured. Glass slide and attached material from 1-day-old 0.5 water:cement specimen.

Fig. 4. Paste side of 3-day-old 0.5 water:cement specimen showing hollow-shell grain in center. Note portion of duplex film carried with paste, lower right corner.

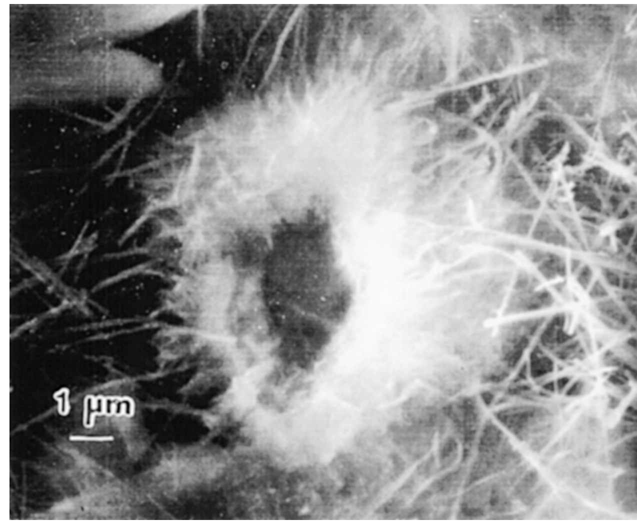

Fig. 6. Completely hollow grain on paste side of 28-day-old 0.5 water: cement specimen.

The youngest specimen Hadley examined had been hydrated for 1 day. In his 3-day-old specimens Hadley found many fractured hollow hydration shells and remarked that there was no appreciable filling of the interior voids between 1 and 3 days; to the contrary, the hollowing out process seemed to continue. However, the cement paste had hydrated further and was more cohesively bound, and some of the individual hollow-shell grains were pulled away to the paste side rather than the glass substrate side during the separation. An example is shown in Fig. 4, which was taken from the separated paste rather than from the substrate. A portion of the duplex film that had been well bonded to the paste and remained with the paste side when the separation took place is visible in the lower right corner of the figure.

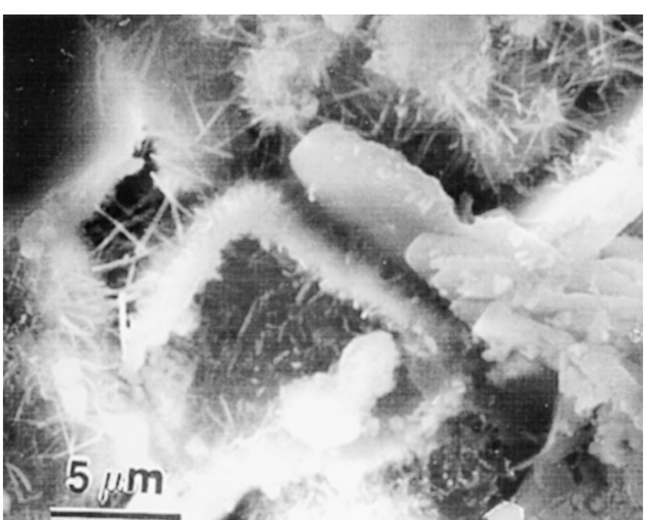

Fig. 5. Completely hollow-shell grain exposed on paste side of a 14-day-old 0.5 water:cement specimen. Note a piece of the covering duplex film in the upper left corner.

Between 3 days and 14 days the bond between the duplex layer deposited on the glass slide substrate and the rest of the cement paste had grown stronger. As a result, for 14-day-old specimens only a few small isolated areas of interfacial film remained on the substrate side after separation. Most of the duplex film remained with the paste and formed an intact cover, hiding the details of the paste. However, the coverage of the paste surface by the duplex film was not quite complete, and Hadley examined the bulk paste through the occasional gaps or windows in the duplex film. He noted that fractured empty hydration shells, little changed in appearance from those found in earlier samples, were prominent. An example is provided in Fig. 5. A bit of the duplex film is visible in the upper left corner of the figure.

Finally, even in specimens 28 days old, Hadley noted that hollow-shell grains continued to occur. Fig. 6 is such a shell. Hadley noted that

> Dimly seen within this hollow body is an acicular crystal projecting to the center of the void and indicating that the cement grain that initially filled the cavity has completely dissolved. There is no indication of additional deposition of material within the shell other than the acicular crystal.

The acicular crystal in question is clearly visible on the original micrograph but may not be visible in the printed figure.

4. Occurrence of hollow-shell grains with laboratory preparations other than Portland cement pastes

Specimens similar to those described above were prepared from 0.50 water:binder pastes made from alite alone, from a mixture of alite and 2% gypsum by weight, and from a mixture containing alite, 2% gypsum, and 13% C_3A.

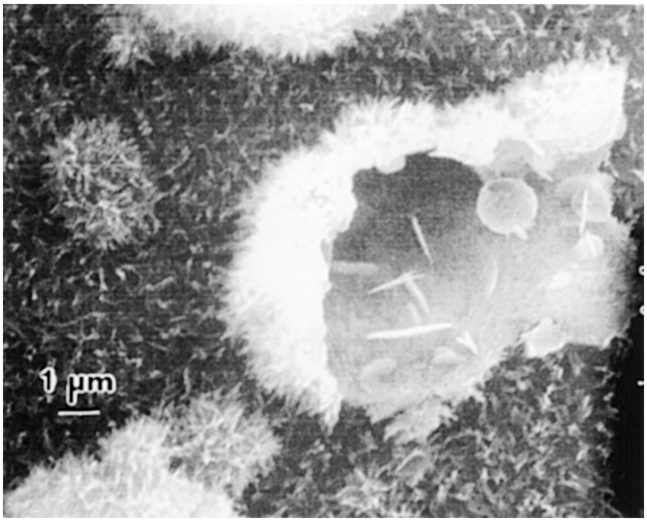

Fig. 7. Ruptured hollow-shell grain on glass substrate side of 3-day-old specimen of alite paste (0.5 water:cement) cast against glass. The few crystals visible in the interior space appear to be thin plates rather than ettringite rods. Most of the figure shows the "inner" or C-S-H side of the duplex film, in contrast to the "outer" or CH side shown in Figs. 5 and 6.

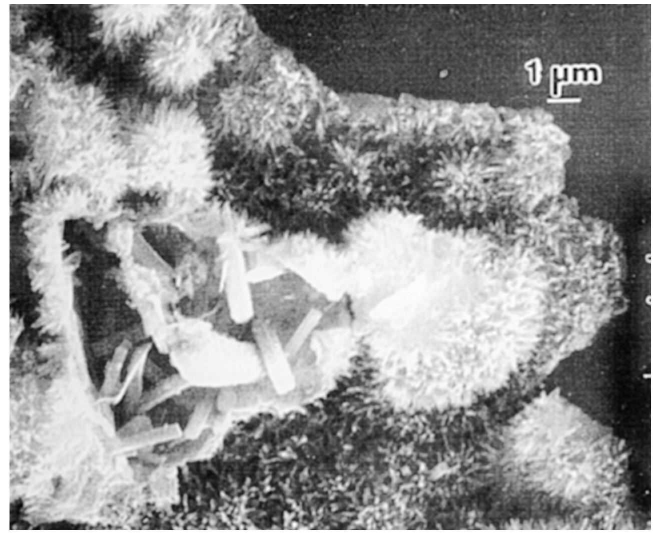

Fig. 8. Ruptured hollow-shell grain on glass substrate side of 3-day-old specimen of alite + gypsum paste (0.5 water:cement) cast against glass. The stubby rods are presumably ettringite. Note the small residual alite grain in the center. The "inner" or C-S-H side of the duplex film is visible over much of the field. The black area in the upper right portion is glass.

All of the materials were ground to cement fineness prior to mixing. Specimens were examined after 3 days of hydration.

Hadley found ruptured hollow shells on the substrate side of a 3-day-old alite paste specimen prepared without gypsum. As indicated in Fig. 7, thin platy crystals, rather than rod-shaped crystals, were visible in the interior space. These were oriented roughly perpendicular to the shell covering. Hadley presumed that these may represent C_4AH_{13} crystals derived from the aluminum impurity in the alite.

A corresponding hollow-shell grain from the 3-day-old alite-gypsum paste is shown in Fig. 8. The interior acicular crystals were considered to be possibly ettringite, but no sulfate was detected in energy-dispersive X-ray examinations. This may be due to the difficulty of receiving X-ray signals from such thin, isolated acicular crystals.

Finally, Fig. 9 shows a hollow-shell grain in 3-day-old alite-gypsum-C_3A paste. Here sulfur and aluminum were both detected.

It appears that hollow-shell formation is not restricted to cement per se, but occurs to some limited extent with alite alone, and certainly with alite-gypsum and alite-gypsum C_3A mixtures. Ettringite formation does not seem to be a necessary feature of this mode of hydration.

5. Occurrence of hollow-shell grains in bulk cement paste

Hadley recognized the importance of attempting to establish the extent to which hollow-shell hydration grains might be found in bulk cement paste or concrete, but was unable to do so. He indicated that:

> An important question is whether the hollow shells occur throughout the body of cement paste, or are restricted to the immediate vicinity of the aggregate. Many fracture surfaces of bulk paste were examined. No hydration shells of the type under discussion were recognized. The structure of bulk paste is however so massive, especially in older pastes, that the recognition of individual morphological units of the type observed near the interface is difficult. Thus, while no hollow hydration shells were found within the bulk paste, neither were any *filled* hydration shells or "pseudomorphous grains" as described by Williamson and [by] Diamond.

Hadley also left open the question of whether hollow shells persist at later ages, since the oldest specimens he examined were only 28 days old.

6. A brief review of findings of hollow-shell grains subsequent to Hadley's thesis

Subsequent to the completion of Hadley's investigations, further work on hollow-shell hydration was carried out at Purdue University by Bobby D. Barnes. In his Ph.D. thesis, completed in 1975 [3], Barnes showed by careful examination that hollow-shell hydration grains were not confined to interfacial regions, but occurred extensively in bulk cement pastes and in bulk mortars. He examined specimens prepared from ASTM cements of Types I, II, III, and V, and found hollow-shell hydration grains as characteristic features in all of them. The conclusion that hollow-shell hydration grains were a general feature to be expected in pastes

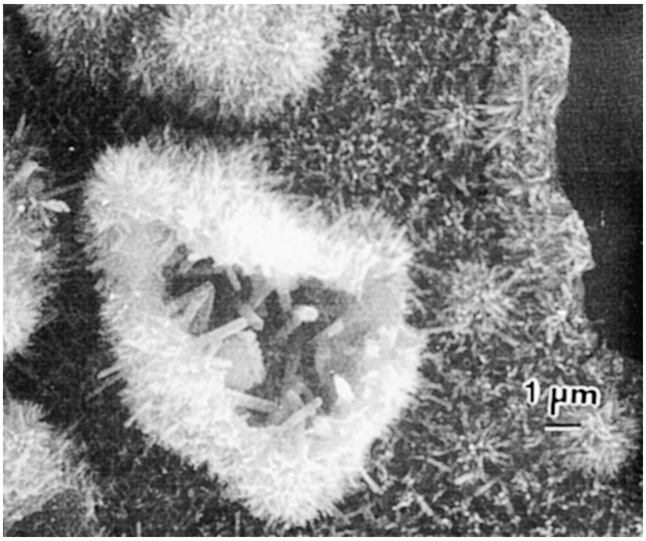

Fig. 9. Ruptured hollow-shell grain on glass substrate side of 3-day-old specimen of alite + gypsum + C_3A paste (0.5 water:cement) cast against glass.

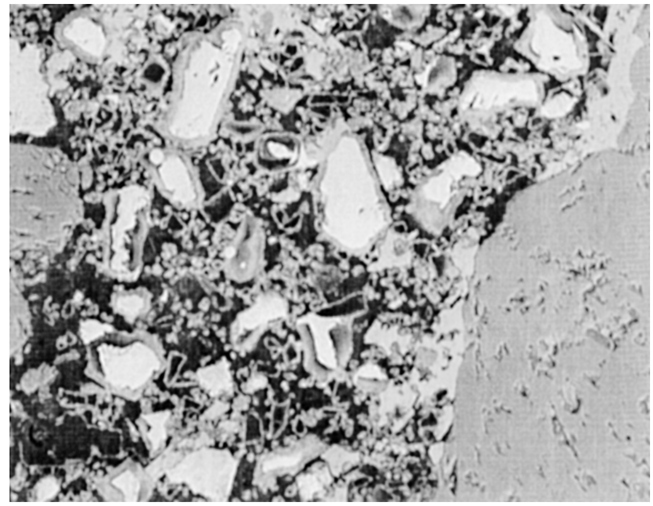

Fig. 10. Backscatter SEM from a 3-day-old 0.5 water:cement concrete showing various hollow-shell hydration grains.

and concretes prepared from a wide range of cements was published by Barnes et al. [4] in this journal in 1978.

The detection of hollow-shell hydration grains in cement pastes or concretes was very much a hit-and-miss affair as long as surfaces for SEM examination were exposed by fracture, a necessary feature with secondary mode SEM. The only way the interior of a particular grain could be visualized was if that grain happened to be cleaved by fracture in the SEM specimen preparation process.

The more recent development of backscatter mode SEM detectors changed things drastically. Such detectors permit examinations of arbitrary plane surfaces generated by slicing specimens with a saw, instead of fracturing them. This mode of examination provides a cross-sectional view through all of the structural elements present on the plane—a much more satisfactory procedure for many purposes.

As more and more published backscatter images of pastes, mortars, and concretes appeared in the literature, it became obvious that hollow-shell hydration grains were indeed a characteristic feature of the cement hydration process. An example of a concrete micrograph exhibiting many hollow-shell hydration grains is provided as Fig. 10.

There has been some confusion over the years as to whether a hollow-shell grain (or a “Hadley grain”) had to be completely hollow to qualify for the designation. It is evident that the “hollowing out” process may take considerable time (i.e., weeks or months); in the usual view it is the hollowing out *process* that defines hollow-shell grains, not the stage of the process in a particular grain. It has also been suggested by various workers that the hollow grains have a limited lifetime and may be filled in rapidly by hydration products. However, examination of mature pastes and concretes over the years has indicated that many hollow-shell grains in mature concretes are, and remain, completely empty. This is not unexpected; indeed, Hadley [1] indicated that “by 28 days many of the hydration shells are completely hollow.”

Fig. 10 is an attempt to show the nature of the hollow-shell formation process as part of the normal development of hydrating cement paste. The specimen is a 3-day-old plain 0.50 water:cement concrete from a typical composition ASTM Type I cement. The concrete is badly mixed and the area is highly porous. There are a number of partly empty hollow-shell grains with bright cores of unhydrated material and a significant number of smaller, fully empty shells. Some of the finer pores in the groundmass structure also appear to be small rimmed pores. It appears that these may have been derived from smaller cement grain fragments that hydrated much more quickly than the coarse grains.

It also appears that some of the pores detectable by SEM in this concrete, and in all normal concretes, are not *capillary* pore space by the standard definition. Capillary pore space is ordinarily taken to represent the residue of originally water-filled space between cement grains. The hollow-shell pores represent not this, but rather space generated by the hollowing-out process of Hadley grain formation within formerly solid cement grains.

It would be of great interest to quantify the proportions of the two kinds of pore space. Image analysis techniques can readily isolate, quantify, and size all of the pores that are large enough to be observed, but to the writer’s knowledge, no program has yet been written to distinguish hollow-shell pore space from capillary pore space of the same size range.

However, in silica fume-bearing concrete it is commonly observed that that the sizes of the capillary pores are smaller than usual, and that they are further reduced with progressive hydration. Many pores derived from hollow-shell

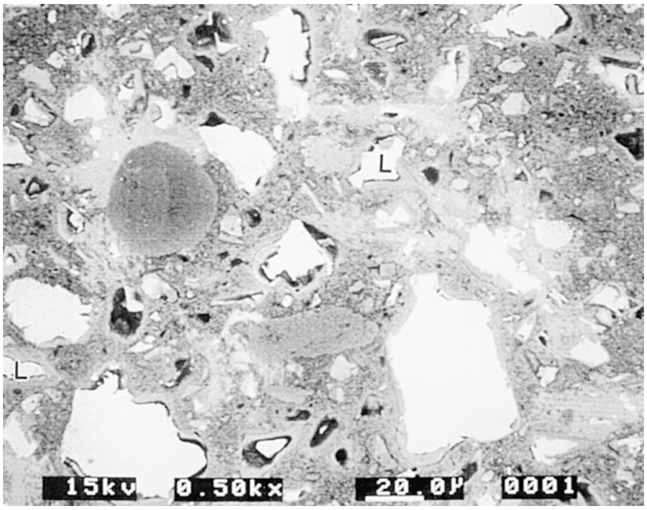

Fig. 11. Backscatter SEM from a 3-day-old silica fume-bearing cement paste, 0.4 water:binder, incorporating 10% silica fume and a 1% dosage of superplasticizer, and showing the distinction between large hollow-shell pores and much finer capillary pores in such systems.

grains mostly remain in the size range commensurate with cement grains (i.e., of the order of perhaps 5 to 20 μm). Accordingly, in such concretes they are easily distinguished from the much finer capillary pores. An example is shown in Fig. 11, from a 0.45 water:binder paste with 10% silica fume, hydrated for 3 days. The field includes more than half a dozen fully hollow Hadley grain spaces and many others in various stages of dissolution of the cores.

Kjellsen et al. [5] have taken advantage of this feature of silica fume-bearing pastes to estimate the hollow-shell pore content. In their pastes the bulk of the non-hollow-shell pores were below the limit of detection of the image analysis system, especially for the more mature pastes. They found that the area percent of pore space derived from Hadley grains (which constituted all of the pores that could be detected) ranged from a few percent to as much as 9%, in different mixes.

7. Conclusions

The occurrence of hollow-shell hydration grains as a significant feature of the hydration process in bulk cement pastes and concretes was demonstrated as early as Hadley's thesis in 1972, and is repeatedly confirmed in current SEM studies. For various reasons the importance and universality of phenomenon has been widely ignored. The present paper provides a historical context that may be useful in disseminating wider understanding of the existence of this mode of cement hydration.

Acknowledgments

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