Pergamon

Cement and Concrete Research, Vol. 26, No. 4, pp. 593-599, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00031-2

EVIDENCE OF HOLLOW SHELLS IN THE MICROSTRUCTURE OF CEMENT PASTE

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(Refereed)
(Received November 30, 1995; in final form January 23, 1996)

ABSTRACT

Experimental evidence in support of hollow shells in the microstructure of cement paste is presented. The experimental observations show that hollow shells are not artifacts caused by drying or particle pull-outs, but are actually an important mode in the hydration of cement.

Introduction

There are indications that the microstructure of cement based materials are much more diversified than suggested by the early microstructural models proposed by Taplin (1) and Powers (2), which predicted the formation of "outer" products, and "inner" products. This model is still widely accepted and adopted. Hadley (3), in his study of the microstructure, observed that at early hydration stages a shell of hydration products formed on the hydrating cement grains. As the cement grains continued to hydrate a progressively larger void space developed within the shell. Many of these hydration shells eventually became completely hollow, while others contained remnant anhydrous cement particles. Later, such hollow shells, or Hadley grains as they also have been termed, have been observed and discussed by several researchers (4-9). The observations of hollow shells challenges the early model that inner products develop in close contact with hydrating cement grains and outer products. In discussions with colleagues over the years we feel that hollow shell hydration has not been widely accepted as an important mode of cement hydration, but is rather considered to be a peculiar hydration mode occurring only under some circumstances.

Scrivener (10) has described the microstructure of cement-based materials in some detail. She summarizes numerous observations of fracture surfaces and polished sections and observes that by 10 hours of hydration, the reaction of C_3S produces "outer" product C-S-H on the AFt rod network, leaving ~1 micron between the grain surface and hydrated shell. At about this time (10,11), the bonds between outer shells is strong enough to expose unreacted particles on fracture surfaces. Continued hydration reduces separation of anhydrous grain and hydrated shell (10).

The origin of hollow shells are sometimes attributed to artifacts of specimen preparation, including shrinkage and opening of the void space due to drying and particle pull-out during fracture or polishing.

Most observations of hollow shells have been carried out in the scanning electron microscope (SEM) on fractured surfaces. It is, of course, possible to argue that the population of grains that are fractured so as to expose their interior microstructure is not representative of the total population, but rather is biased in favor of hollow shells, as was pointed out by Barnes et al. (4). It is also likely that remnant anhydrous grains are pulled out during fracturing of the specimens, thus revealing a completely hollow shell (12). It has also been argued that hollow shells might be artifacts of the severe drying that the specimens undergo prior to, and during, SEM examination, i.e. Dagleish et al. (5,11).

At present, two questions have not been fully answered: 1) Is hollow shell hydration a genuine mode of hydration or are they artifacts of specimen preparation? and 2) If they are not artifacts, are they a common feature in the microstructure or are they exceptional and relatively unimportant? The objective of the present work has been to answer these questions. The experimental methods included environmental scanning electron microscopy (ESEM) and scanning electron microscopy (SEM).

Experimental

Materials. Specimens were made of portland cement, condensed silica fume, deionized water and a superplasticizer. The cement used was a Swedish low alkali sulfate resistant cement (corresponds to ASTM TypeV). The silica fume was in slurry form and contained 50% solids. The characteristics of the cement and silica fume is given elsewhere (13). The plasticizer was composed of 40% sulphonated naphthalene formaldehyde, 0.3% tribetyl phosphate and water. Pastes of water/binder (w/b) ratios 0.25, 0.30 and 0.55 were produced. The binder of the two 0.25 w/b ratio pastes were composed of 100% cement or 90% cement and 10% silica fume, by weight. The mass of superplasticizer was 3.0 or 4.0%, respectively, of the binder weight. The 0.30 w/b ratio paste contained 5% silica fume and 2.0% superplasticizer. The 0.55 w/b ratio paste contained only cement and water.

Details of the mixing procedure is given in (13). The curing temperature was 20°C. The paste was cast in molds having 12 mm compartments. In order to prevent segregation of the paste before the forms were opened, the molds were completely sealed and rotated under water for at least 12 hours. Specimens were placed in tightly sealed glass bottles containing only a very small amount of air. This ensured sealed curing conditions with practically no moisture exchange or carbonation.

Methods. SEM backscattered electron (BSE) images of flat polished specimens were obtained. The Jeol 6400 SEM was operated at 10 kV and the working distance was 8 mm. The SEM was operated both in the compositional (COMP) and the topographical (TOPO) backscattered electron modes, the latter obtained by subtraction of the signals from the semiconductor element detector. The more common compositional imaging is obtained by addition of the signals. Energy dispersive X-ray analyses (SEM-EDX) were also performed in order to identify various phases.

The ESEM maintains most of the advantages of the SEM, however, the specimen chamber in an ESEM is operated at high relative humidities. Indeed, the specimen temperature and the

specimen chamber pressure can be regulated so that relative humidities ranging from 100 to almost 0% are maintained. The accelerating voltage was held at 20 kV. The Peltier cooling stage was applied to cool the specimen to 10°C in the microscope during operation. The microscope was operated at pressures, providing relative humidities around the specimen in the range 90 to 10%. Reviews describing the principles and functions of the ESEM in more detail are given elsewhere (14,15).

Specimen Preparation. Before the ESEM examination, the cubes were cooled to 10°C and fractured in tension, and then immediately attached to the Peltier cooling stage by rubber cement. The fractured surfaces were examined. After the specimens were mounted, the specimen chamber was pumped down to 8.5 torr while the specimen was maintained at 10°C, providing a relative humidity of approximately 90%.

Regarding the specimen for SEM imaging, the hydration was stopped by freeze-drying. Specimens of 1 to 2 millimeters were sawn out of the cast cubes by a diamond precision saw and subsequently submerged in liquid nitrogen before vacuum dried for 2 days. After the drying procedure, the specimens were vacuum-impregnated with a low-viscosity epoxy resin and very carefully ground and polished down to 0.25 microns. Alcohol was used as lubricant during cutting and grinding while diamond paste was the polishing compound. The SEM specimens were finally coated with carbon. Note that the epoxy impregnation was performed prior to grinding and polishing.

Results and Discussion

Environmental Scanning Electron Microscopy (ESEM). Fig.1 shows an ESEM image of the 0.55 w/b ratio paste after 2 weeks of hydration, at a relative humidity of 50%. An example of a hollow shell is seen in the central part of the image. A fractured hydration shell revealing the interior of the hollow shell is observed. A remnant core is seen inside the shell. Outside the

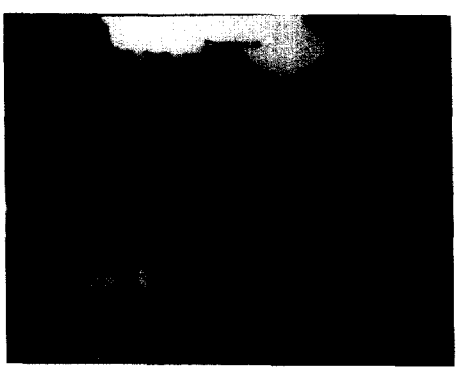

FIG. 1.
ESEM image of a 2 weeks old cement paste specimen (w/c ratio 0.55) at a relative humidity of 50%. Magnification X 4000.

FIG. 2.
ESEM image of a 2 weeks old cement paste specimen (w/b ratio 0.30) at a relative humidity of 90%. Magnification X 1950.

shell, to the right, capillary pore space is observed clearly. Examination of hollow shells has shown that a moderate drying of the specimen from 90 to 50% RH in the microscope has no apparent effect on the appearance of the hollow shells. Even drying down to 10% RH has apparently no effect on the appearance of hollow shells. The only influence on the microstructure of drying from 90 to 10% RH, was a widening of microcracks (13). The hollow shell observed in Fig.1 by ESEM at relatively high humidity is similar to those previously observed by SEM under vacuum (5,6).

Fig.2 depicts an ESEM image of the 0.30 w/b ratio paste after 2 weeks of hydration. A large hollow shell is seen in the central part of the image, at a relative humidity of 90%, and before any external drying. The hollow shell apparently contains a remnant anhydrous grain. In contrast to the hollow shell observed in Fig.1, a distinct hydration "shell" can not be distinguished, presumably because of intergrowth of hydration products in the originally water filled space. Rather than a distinct hydration shell, a dense mass of reaction products is observed surrounding the anhydrous core, with an intra-shell void, separating the anhydrous core and the dense phase of reaction products. Such dense continuous product phases, with capillary pores too small to be easily resolved by SEM/ESEM is to be expected at low w/b ratios after 2 weeks of hydration. The term capillary pore is used here in accordance with the definition of Verbeck (16). (He explained that the part of the original water space which has not become filled with hydration products at a certain time constitute the "capillary" pore system). Drying of the specimen at 10% RH for 40 minutes inside the ESEM had apparently no effect on the hollow shells. Many other hollow shells were observed in the specimens. The ESEM observations demonstrate that the observed hollow shells are not due to external drying.

Scanning Electron Microscopy (SEM). Fig.3 shows a compositional backscattered electron image of the 0.25 w/b ratio paste without silica fume hydrated for 12 hours. The cement grains appear almost white, CH appear light gray, C-S-H appear generally as darker gray while pores appear black in compositional BSE images. It can be observed that reaction products have formed rather homogeneously throughout the originally water filled space. The presence of

FIG. 3.
SEM-BSE image (compositional) of the 0.25 w/b ratio paste without silica fume hydrated for 12 hours.

FIG. 4.
SEM-BSE image (compositional) of the 0.25 w/b ratio paste without silica fume hydrated for 1 day.

FIG. 5.
SEM-BSE image (compositional) of the 0.25 w/b ratio paste containing silica fume hydrated for 1 day.

hollow shells are not apparent at this stage. Fig. 4 shows the same mix after 1 day of hydration. The hydration has continued, resulting in a densification of the originally water filled space by continued deposition of reaction products. Some larger apparently empty pores are seen as well as voids separating the phase of reaction products and several cement grains. Voids are filled with epoxy and, as will be shown later, they are not the result of specimen preparation. The majority of the smaller cement grains observed at 12 hours of hydration are not seen after 1 day; the smaller cement grains observed at 12 hours have completely reacted and left hollow shells with the same size and shape as the smaller cement grains. Some of these completely hollow shells are marked with white arrows. It is important to note that the majority of the larger voids at 1 day of hydration (Fig.4) are larger than any of the pores at 12 hours of hydration (Fig.3). The pores get larger during the first day or so as a result of the formation of Hadley grains. The size and shape of pore indicates that they were once filled with unreacted cement.

Many of the smaller cement grains, particularly alite and aluminate, will hydrate completely by one day, thus leaving completely hollow shells. Larger cement grains will not have hydrated completely at the same age, thus leaving hollow shells with remnant anhydrous cores. The larger hollow shells containing remnant anhydrous cores observed in Fig.4 are similar to that observed from the ESEM image in Fig.2. Some of the hollow shells containing remnant anhydrous cores are marked with black arrows. It is possible that some of the apparently completely hollow shells are, in fact, the bottom or top of larger hollow shells containing remnant cores. On continued hydration, the hollow shells with remnant anhydrous grains may develop into completely hollow shells or they may refill with fresh hydration product (10).

A compositional backscattered electron image of the 0.25 w/b ratio paste containing silica fume hydrated for 1 day is shown in Fig.5. Examples of completely hollow shells are marked with white arrows while examples of hollow shells containing remnant anhydrous cores are marked with black arrows. Fig.6 is a topographical backscattered electron image of the same area as in Fig.5. Some topographical relief is inevitable in flat polished cementitious specimens and results from the polishing of different hardnesses of various phases. The larger hollow shells as seen from Fig.5, which are similar to those seen in Fig.4, are effectively filled with

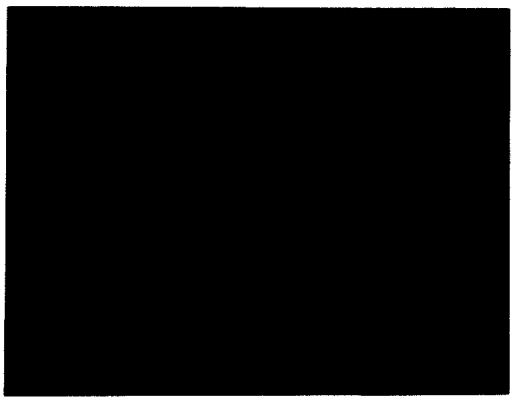

FIG. 6.
Topographic SEM-BSE image of the same area as shown in Fig.5.

epoxy. If these larger pores were not impregnated with epoxy they would have been observed as deep cavities in the topographical image. Since the impregnation of epoxy was done prior to grinding and polishing, it is evident that any grains or solid material have not been pulled out of these larger pores. Obviously, the inside of the hollow shells are connected to the original surfaces of the specimens by pores large enough to allow the epoxy to pass.

By studying many images similar to Fig.5, one finds intra-shell separations are observed around larger alite grains (a), but never around belite grains (b) and seldom around the ferrite phases (f). After one day, there is close contact between the phase of reaction product and belite grains. Our results indicate that hollow shells do not only exist, but that hollow shell hydration is the general hydration mode of the examined specimens at relatively early ages. These results will be reported at a later stage.

Conclusions

Hollow shell hydration has been studied. Environmental scanning electron microscopy indicate that hollow shells are not the result of drying. Standard scanning electron microscopy studies of epoxy impregnated flat polished specimens has shown that hollow shells are not a result of particle pull-out. Hollow shells are a common mode of hydration.

Acknowledgments

We acknowledge the financial support provided by the Swedish research consortium of high performance concrete structures. The group consist of Cementa, Elkem Materials, Euroc Beton, NCC, Skanska, Strängbetong, and the government authorities BFR and Nutek. We would also like to thank Marina Reider and Nora Dahle who assisted in the microscopy. Support of the environmental scanning electron microscopy is provided through grants from the Department of Energy (award No. DE-FG02-91ER45460/A02) and the NSF Science and Technology Center for Advanced Cement-Based Materials (award No. DMR 9120002).

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