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Investigating entrained air voids and Portland cement hydration with low-temperature scanning electron microscopy

David J. Corr [a,*], Maria C.G. Juenger [b], Paulo J.M. Monteiro [c], Jacob Bastacky [d]

[a] *Department of Civil and Environmental Engineering, Northwestern University, Technological Institute Suite A130, Evanston, IL 60208, USA*
[b] *Department of Civil Engineering, The University of Texas at Austin, 1 University Station C1748, Austin, TX 78712-0275, USA*
[c] *Department of Civil and Environmental Engineering, University of California, Berkeley, 725 Davis Hall, Berkeley, CA 94720, USA*
[d] *Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, CA 94720, USA*

Abstract

This paper describes the application of low temperature scanning electron microscopy to the materials science of Portland cement. The details of low-temperature scanning electron microscopy are described, along with a number of specimen preparation techniques. There are three main research topics presented in this paper: (1) ice morphology in entrained air voids, (2) development of air voids during early hydration and (3) progression of hydration in Portland cement. The first research focus examines ice in air voids at freezing temperatures, and various cement paste ages. The second research focus tracks the development of the air voids during the first hour of hydration. In the third research focus, the progression of hydration with and without accelerating and retarding admixtures is described. Each of these research programs demonstrates how low-temperature scanning electron microscopy can be an effective tool in Portland cement research.

Keywords: Microscopy; Ice formation; Cement hydration; Entrained air voids; Low-temperature scanning electron microscopy

1. Introduction

Recently completed research programs at the University of California, Berkeley have demonstrated the utility of low-temperature scanning electron microscopy in Portland cement research. The first objective of this research program is to examine the entrained air voids of Portland cement paste, including their development during hydration, and to observe the ice that forms within them during freezing. Portland cement paste (a mixture of Portland cement and water which forms the matrix in Portland cement concrete) is a porous material, with pore sizes ranging across many orders of magnitude. In a humid environment, much of this porosity will be 100% saturated with liquid. Because of this great size range of porosity, and the resulting differential in freezing points among the saturated pores, Portland cement paste is highly susceptible to the expansive degradation caused by freezing and thawing cycles. The mechanisms of this degradation are complex and not fully understood (see [1] or [2] for details). Hydraulic pressure and osmotic pressure effects cause freeze–thaw damage associated with more than the simple 9% expansion that water experiences during bulk solidification [2].

Whatever the prevailing degradation mechanisms, the introduction of air voids into Portland cement paste is very effective in protecting the paste from damage due to freezing and thawing. Air voids are entrained into the paste by introducing air entraining admixtures to concrete as it is mixed. The active ingredients in these admixtures are anionic surfactants, which stabilize the bubbles that naturally form during the mixing of concrete. These stable bubbles remain through the setting and hardening of the concrete, and eventually become "air voids" in the hardened cement paste. The air voids are typically 50–200 μm in size, and provide a reservoir where water can solidify without causing damaging tensile strains in the brittle cement paste [3]. There is a large body of indirect evidence for this process of ice formation, but direct observation of ice in air voids is scarce. This study aims to fills this gap in the state of

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[*] Corresponding author. Tel.: +1-847-467-2368; fax: +1-847-467-1078.

E-mail addresses: d-corr2@northwestern.edu (D.J. Corr), mjuenger@mail.utexas.edu (M.C.G. Juenger), monteiro@ce.berkeley.edu (P.J.M. Monteiro), jbastacky@chori.org (J. Bastacky).

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knowledge by employing low-temperature scanning electron microscopy to image ice formation in air voids.

Another objective of this research program is to study the progress of hydration in Portland cement paste. One of the inherent difficulties in applying imaging techniques to hydrated or hydrating cement paste is the dramatic differences in morphology that can be seen in the presence or absence of water. In the case of traditional scanning electron microscopy, specimens must be vacuum dried before the imaging process, which occurs in a near-perfect vacuum. Using low-temperature scanning electron microscopy, the specimens are imaged with all of their original water present, stabilized in the vacuum at a cryogenic temperature. With this technique, the orientation and morphology of hydrating particles and hydration products can be observed without alteration from the drying procedure.

2. Experimental techniques and materials

2.1. Low-temperature scanning electron microscope

The low-temperature scanning electron microscope (LTSEM) is closely related to the standard scanning electron microscope, except that the specimen is kept at a cryogenic (−190 °C) temperature during imaging [4,5]. At this temperature, the vapor pressure of water is extremely low ($<10^{-10}$ Torr), and therefore very little ice sublimes from the surface of the sample during imaging. Thus, a hydrated specimen can be quenched in liquid nitrogen and viewed in the LTSEM without the drying procedure normally used with a standard SEM.

The central equipment of the LTSEM experimental setup used in this study is an Amray 1000A scanning electron microscope. This microscope is fitted with a multipurpose cryochamber [6] that allows specimens to be kept cold during specimen preparation and loading into the imaging chamber. A diagram of this cryochamber is given in Fig. 1. The cryochamber has a dedicated vacuum system, separate from the microscope vacuum system. Access to the cryochamber is through an airlock system, which allows for specimen manipulation in the cryochamber while maintaining the vacuum.

Specimen preparation involves quenching in liquid nitrogen, followed by mounting onto the specimen holder, while still immersed in liquid nitrogen. After preparation, the specimen holder is transferred to the cryochamber through the airlock system. The cryochamber is fitted with a knife that can be used either to slice the specimen, or to fracture it, both of which allow the interior of the specimen to be imaged. A coating fixture can be mounted through the cryochamber airlock system to coat the fractured specimen with a layer of conductive material (carbon or gold) to prevent surface charging.

Once the specimen is fully prepared, it is inserted into the microscope chamber, with the transfer mechanism shown in Fig. 1. The microscope is fitted with a cryostage, which employs a Joule–Thomson refrigerator to maintain the cryogenic temperature of the specimen during imaging. The Joule–Thomson refrigerator works by forcing pressurized nitrogen through a small orifice; past this orifice, the gas expands rapidly and drops in temperature, cooling the stage to the operating temperature of −190 °C. Stopping or reducing the gas flow through the Joule–Thomson refrigerator allows the specimen to be warmed while in the microscope chamber. This allows the user to image the same locations before and after sublimation of ice.

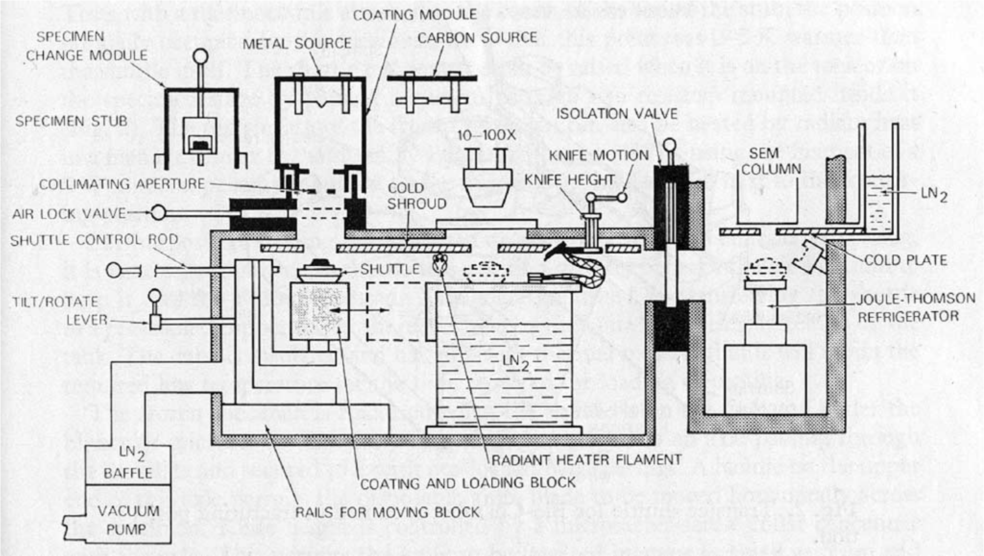

Fig. 1. LTSEM cryochamber (after [6]).

2.2. Specimen preparation

In this section, three LTSEM specimen preparation techniques are discussed, along with the cement paste mixture designs used for each technique. In all cases, the Portland cement is an ASTM Type I cement.

2.2.1. Mature cement paste specimens

For the mature cement paste specimens, the mixture design is as follows: water-to-cement ratio of 0.45, and a replacement of 18.5% of the deionized mixing water with a commercial air entraining admixture. These specimens are cast in plexiglass molds, 8 mm × 7 mm × 2 mm in size, with a notch molded along the 8 mm axis to facilitate fracture in the cryochamber. For the purposes of this study, "mature" specimens are considered to be over 1 day old, or fully set cement paste. The purpose of these specimens is to study the ice morphology inside the entrained air voids of frozen cement paste. The specimen ages and curing conditions vary; these are given below for each specimen. All mature specimens are frozen at a normal climatic temperature of −7 °C before the liquid nitrogen quenching during LTSEM preparation. With this procedure, the ice present in the air voids at −7 °C is preserved throughout the specimen preparation and is observable in the LTSEM.

2.2.2. Fresh cement paste specimens

The second type of specimen for air void characterization is a "fresh" cement paste, with the following mixture design: water-to-cement ratio of 0.4, pure surfactants sodium dodecyl benzene sulfonate or sodium oleate added as 0.5% weight percent of the deionized mixing water. For these experiments, specimens are mixed by hand for 5 min and cast into the same plexiglass molds as the mature specimens. The entire mold is then quenched in liquid nitrogen. The mold is disassembled while still immersed in liquid nitrogen, and the specimen extracted. From here, the specimens are mounted on specimen holders and fractured in the cryochamber in the same manner as the mature cement paste specimens.

The result of the liquid nitrogen quenching in this procedure is that the specimen freezes quickly, reaching −190 °C in approximately 10 s. Because this freezing process is so rapid and proceeds to such a low temperature, the pore water in the fresh paste does not undergo the crystal nucleation and growth processes typically associated with water solidification. Instead, the rapid cooling gradient causes the formation of ice "micro-crystals" that are not visible in the LTSEM [7]. The cement grains and air voids are suspended in their locations at the 5-min hydration states, and can be viewed in the LTSEM in their original configuration during early hydration.

Specimens used for hydration studies are also "fresh" cement pastes, with a water-to-cement ratio of 0.45% and 1% (by weight of cement) additions of calcium chloride or sucrose. The sample preparation is as described above, except that only 3 min is allowed for mixing and casting before quenching in liquid nitrogen. They are fractured with the cryochamber knife and coated with a thin layer of gold before imaging.

2.2.3. Glycerol method

The "glycerol method" is a procedure that allows for the isolation of air bubbles from fresh cement paste. The mixture design used in this procedure is identical to the fresh cement paste specimens. A schematic diagram of the glycerol method is given in Fig. 2. A small amount of fresh cement paste is placed at the bottom of a cylindrical chamber. A 5 cm layer of glycerol is placed above the cement paste, followed by a 5 cm layer of deionized water. The glycerol acts as a barrier between the cement paste and the water, through which the air bubbles can travel without contamination from the water. The cement paste is slowly mixed to allow the bubbles to escape while maintaining a stable water–glycerol interface. The bubbles float through the glycerol and through the water, collecting on the surface of the water. The bubbles can be extracted as a slurry, collected on a specimen

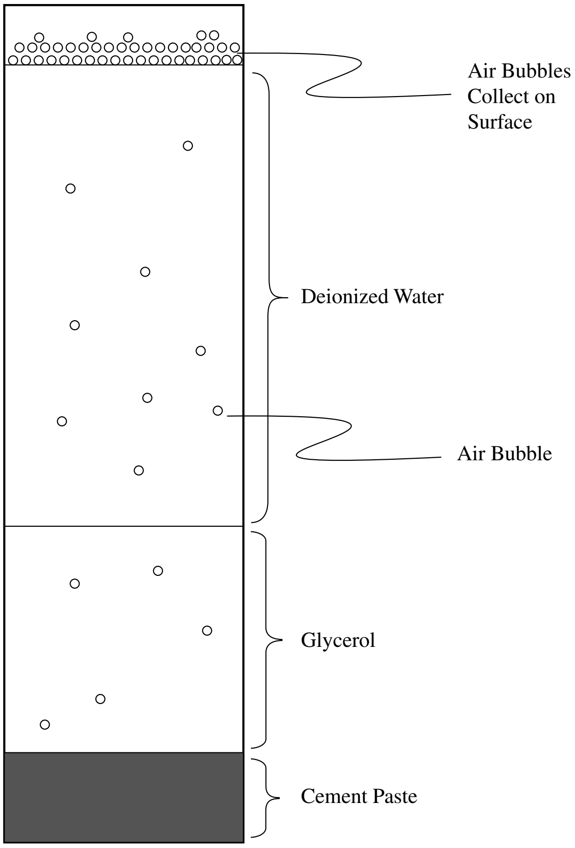

Fig. 2. Glycerol method (after [1]).

holder and quenched as above, then imaged in the LTSEM. With this procedure, the cryochamber knife is used to shave the top layers of the frozen slurry, allowing the interior of the air bubbles to be examined. With the glycerol method, the air bubbles originate from cement paste hydrated for less than 30 min.

3. Results and discussion

3.1. Ice morphology in entrained air voids

Although there is a multitude of indirect evidence of ice formation in the air voids of hardened cement paste, there has been little experimental work to directly examine the presence and morphology of ice in these air voids. This section will give a brief introduction to a recently completed research program designed to fill this gap in the state of knowledge.

An image of an entrained air void from a mature cement paste specimen is shown in Fig. 3. This specimen was cured at 100% relative humidity for 7 days before freezing at −7 °C for 24 h prior to imaging. Fig. 4 shows the same air void after sublimation of the ice; comparison between these two figures indicates which crystals in Fig. 3 were ice crystals. The ice crystals in Fig. 3 are discrete crystals, not a single crystal completely filling the void. These discrete crystals appear to coincide with locations of divots in the air void wall in Fig. 4. These divots could be the outlet of capillary channels, where water typically cannot solidify due to capillary restrictions [8]. This suggests that water flows through the channels to the air void and solidifies upon arrival. It is also possible that these divots are favorable heterogeneous nucleation sites [9] for water entering the void from the surrounding paste. These results confirm the formation of ice in the entrained air voids of hardened Portland cement; further details of this research can be found in [10].

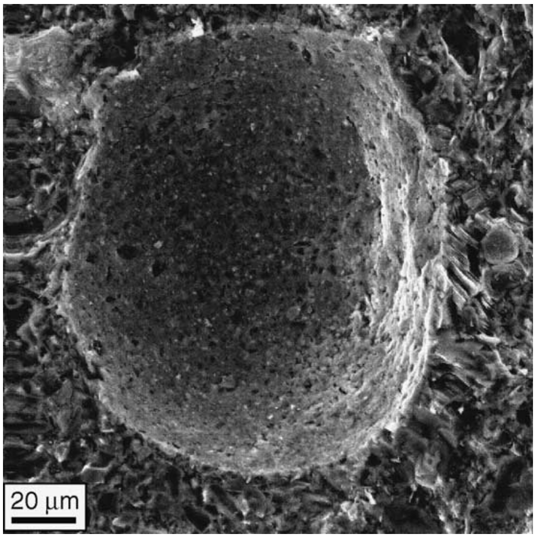

Fig. 4. Same location as Fig. 3 (after sublimation).

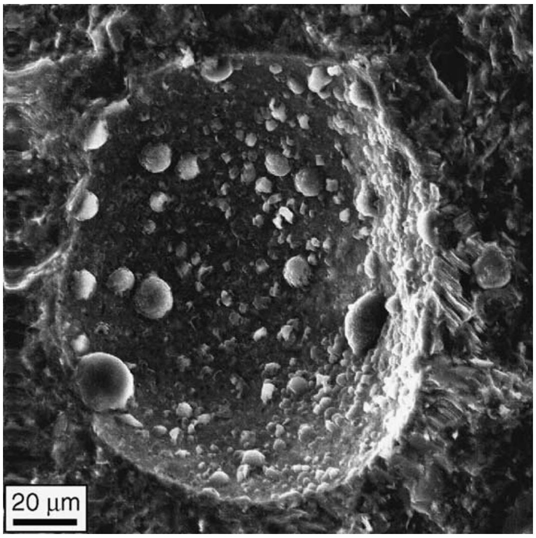

Fig. 3. Discrete ice crystals (before sublimation).

3.2. Air void development

In this section, results from fresh cement paste specimens and glycerol method specimens are shown to demonstrate the development of the air void system during early hydration. Fig. 5 shows an air void and the surrounding cement paste from a fresh cement paste specimen. Sodium dodecyl benzene sulfonate is the air entraining agent used in this specimen, which hydrated for 5 min before being quenched in liquid nitrogen. Fig. 6 shows the same location after sublimation of ice in the LTSEM chamber. There are a few important features to note from Figs. 5 and 6. First, there is a distinct shell to

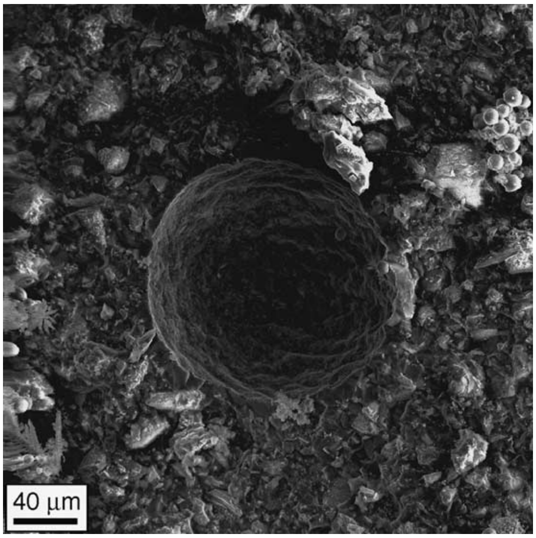

Fig. 5. Fresh cement paste specimen: air void (before sublimation).

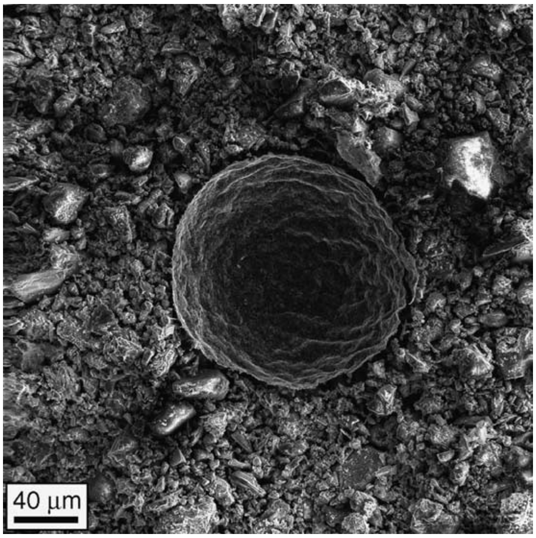

Fig. 6. Fresh cement paste specimen: air void (after sublimation).

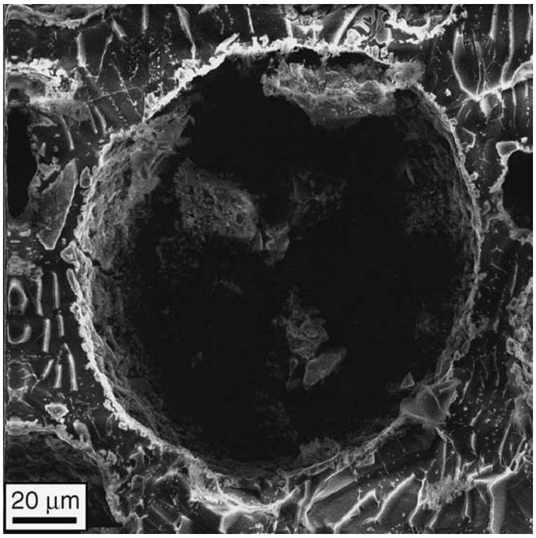

Fig. 7. Glycerol method: air void in slurry (before sublimation).

the air void, which has developed after only 5 min of hydration. It is likely that this shell is due to either the coalescence of fines from the cement paste, or the result of a precipitation between cations in the cement paste and the anionic surfactant molecules surrounding the air bubble. Second, there appears to be a gap between the air void shell and the bulk cement paste. This area is filled with ice in Fig. 5, which has sublimed in Fig. 6. This region around the air void could be due to bleeding effects or packing density effects in the fresh cement paste, or due to the contraction of the air bubble during the liquid nitrogen quenching.

Glycerol method specimens allow for detailed examination of the cohesive structure of entrained air voids. Fig. 7 shows an image of the air void slurry resulting from the glycerol method preparation. In this image, the air void slurry has been sliced with the cryochamber knife, and is still frozen in the LTSEM. As can be seen in this image, the air voids are cohesive enough to survive the glycerol method and liquid nitrogen quenching. Fig. 8 shows a single air void, unsliced by the cryochamber knife, and after the sublimation of ice. This air void, typical of all glycerol method specimens, shows a distinct shell of irregular particles. It is likely that these are preformed particles from the original Portland cement, as hydrates or precipitates would be more uniform in size and shape. A further discussion of the early hydration development of the entrained air voids is given in [11].

3.3. LTSEM examination of hydration

Portland cement hydration can be monitored with low-temperature scanning electron microscopy. Cement paste specimens may be prepared with any combination of chemical admixtures and supplementary cementitious materials. After a brief mixing process, the paste is cast into the previously described small plexiglass molds. The paste may then be quenched in liquid nitrogen and imaged immediately, allowing characterization of very early age hydration products. Alternatively, the sample can be cured for any desired period under any conditions before quenching and imaging. There is considerable flexibility with this technique in terms of the chemistry of the paste, the curing conditions, and hydration time. The hydration process can be monitored by imaging samples from the same mix at different ages. Figs. 9 and 10 show a neat Portland cement paste specimen that was quenched within 3 min of the addition of water to the cement. Hydration products are already visible on the surfaces of the cement grains. Likewise, in specimens containing additions of calcium

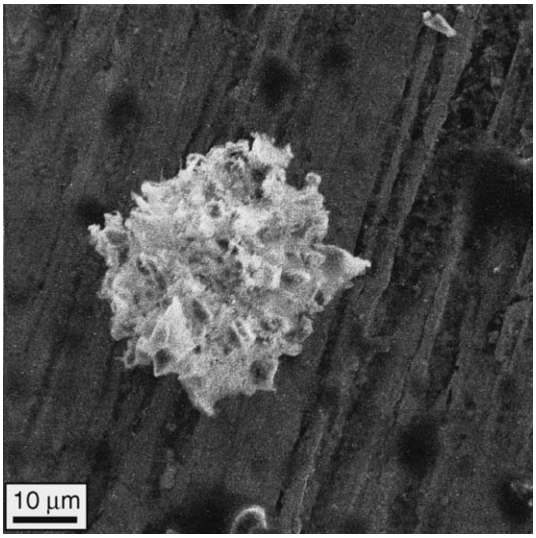

Fig. 8. Glycerol method: pristine air void (after sublimation).

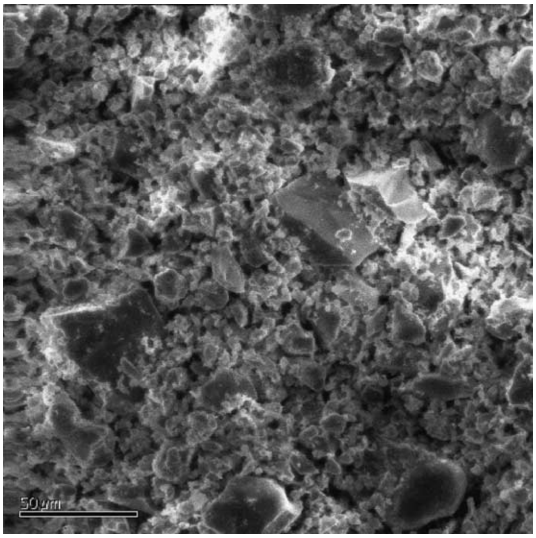

Fig. 9. Hydration investigation (low magnification).

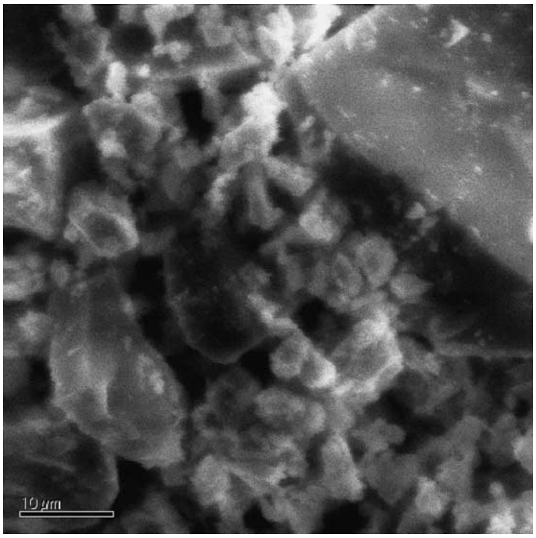

Fig. 10. Hydration investigation (high magnification).

chloride (hydration accelerator) or sucrose (retarder), hydration products are visible after 3 min (images not shown). Monitoring the growth and morphology of hydration products at different times gives insight into the mechanism of chemical acceleration and retardation.

4. Conclusions

The results presented in this paper demonstrate the effectiveness of low-temperature scanning electron microscopy in Portland cement research. In particular, use of the LTSEM has yielded significant results in the following areas:

1. Ice formation and morphology in entrained air voids.
2. Entrained air void development during early hydration.
3. Progress of hydration in Portland cement.

Acknowledgements

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