Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 32 (2002) 1025–1031

Air void morphology in fresh cement pastes

D.J. Corr[a], J. Lebourgeois[a], P.J.M. Monteiro[a,*], S.J. Bastacky[b], E.M. Gartner[c]

[a]Department of Civil and Environmental Engineering, University of California, Berkeley, 721 Davis Hall, Berkeley, CA 94720, USA
[b]Children's Hospital Oakland Research Institute, 5700 Martin Luther King Jr. Way, Oakland, CA 94609, USA
[c]Lafarge, Laboratoire Central de Recherche, 95 rue du Montmurier, 38291 St. Quentin Fallavier, France

Received 7 June 2001; accepted 29 November 2001

Abstract

Two different procedures are used in conjunction with low-temperature scanning electron microscopy to image the air voids in cement pastes at very early ages. The first procedure isolates the air voids from cement paste after less than 30 min of hydration, and allows them to be imaged apart from the paste. The second procedure involves quenching the fresh cement paste specimens in liquid nitrogen after 5 min of hydration. In both cases, a distinct air void shell is apparent even at these short hydration times. The shell appears to be made up of small (1–5 μm) mineral particles. The second method confirms the presence of a water-rich transition zone around the air voids in the quenched pastes, consistent with earlier studies. Foam stability studies show that sodium oleate gives more stable foams than sodium dodecyl benzene sulfonate, but is more sensitive to the presence of calcium ions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; SEM; Freeze and thawing; Admixture; Cement paste

1. Introduction

Air voids are instrumental in the protection of concrete from the deleterious effects of freezing and thawing. As ice forms in concrete, hydraulic pressures are generated both by the increased volume of ice compared with water, and through osmotic and energetic differences between frozen and unfrozen regions. Air voids provide an escape boundary to which water can flow and freeze without generating hydraulic pressures large enough to damage the cement paste. In this paper, factors influencing the formation of air voids during mixing and early hydration of portland cement concrete are examined.

Air voids are entrained into cement paste through the use of surfactants commonly referred to as air entraining admixtures (AEAs). The goal of this paper is to examine the mechanisms by which two common surfactant types entrain air voids into fresh cement paste. We chose to take advantage of low-temperature scanning electron microscopy (LTSEM) techniques first pioneered for cement paste research by Monteiro et al. [1,2], but we extended the scope of these tests with an innovative procedure for isolating the bubbles. The LTSEM allows air bubbles and voids that have been isolated during early hydration to be imaged with their water still present. Rashed and Williamson [3,4] have identified two distinct features to air voids during early hydration: a shell to the air void surface, and a transition zone between this shell and the bulk cement paste. The LTSEM work presented here examines these features in more detail.

2. Materials

Sodium oleate and sodium dodecyl benzene sulfonate (DBS) are the AEAs used in this study. These two molecules represent the major classes of commercial AEA. Other admixtures used are sodium gluconate, a common component of commercial retarders for portland cement concretes, and a commercial superplasticizer based on naphthalene sulfonate formaldehyde condensates (NSFC). ASTM Type I portland cement is used; its composition is given in Table 1. Fly ash types F and C were also used in the foam index test.

---

* Corresponding author. Tel.: +1-510-643-8251; fax: +1-510-643-8929.
E-mail address: monteiro@ce.berkeley.edu (P.J.M. Monteiro).

PII: S0008-8846(01)00751-7

3. Experimental methods

3.1. Foam index test

The foam index test is a simple test that has been proposed to predict both the stability of the air void systems generated through the use of surfactants (AEAs) in concrete, and the level incompatibility of the cement–AEA combination. It is given as follows [5]:

- Dilute surfactant (AEA) in water (1 part surfactant, 20 parts water by volume)
- Combine 20 g cement and 50 mL deionized water in a bottle, cap and shake for 1 min
- Add the diluted surfactant solution to the bottle in 0.2 mL increments from a burette. After each addition, cap the bottle and shake for 15 s. Lay the bottle on its side and observe the stability of the foam in the bottle.
- The amount of dilute surfactant, in milliliters, needed to produce a stable foam, that is, on in which no bubbles can be seen breaking for a period of 15 s, is the foam index of the cement–AEA combination. The higher this value, the lower is the cement–AEA compatibility.

We modified the test procedure for this work. Instead of varying the amount of surfactant, we use a fixed dosage and determine the initial volume of foam after agitation ceases, and that remaining 5 min, both expressed as a percentage of the free volume of the container. This procedure allows us to measure the influence of cement, fly ash, and other additives on the stability of air entrainment at AEA concentrations typical of concrete applications.

3.2. Low-temperature scanning electron microscope (LTSEM)

The LTSEM is closely related to a standard scanning electron microscope (SEM), except that the specimen can be kept at temperatures as low as − 190 °C during imaging. At this temperature, the vapor pressure of water is so low (less than 10^{-10} Torr) that very little water 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 LTSEM is fitted with a multipurpose cryochamber that allows specimens to be kept cold during loading into the microscope. The cryochamber knife can be used to cut or fracture a specimen so that the interior of the specimen can be viewed. The specimen can also be warmed while in the microscope chamber. This allows the user to observe the same locations before and after sublimation of ice. For general information on the LTSEM, cryospecimen techniques, and their uses in portland cement research, the reader should consult Refs. [1,2,6,7].

Table 1
PC-I cement composition

Cement	K_2O (solution)	Na_2O (solution)	CaO (free)	C_3A	C_4AF	C_3S	C_2S
Type I	< 0.24[a]	< 0.21[a]	0.63	3.4	11.4	59.4	17.1

[a] Data given are total amounts; soluble amounts unavailable.

Table 2
Foam index test

Concentrations of surfactants and suspended solids	Elapsed time (min)	Foam remaining (percentage volume)
OL (0.5 g/L)	0	90%
	5	70%
DBS (0.5 g/L)	0	90%
	5	65%
OL (0.5 g/L)	0	45%
and PC-I (w/c = 5)	5	35%
DBS (0.5 g/L)	0	50%
and PC-I (w/c = 5)	5	30%
OL (0.5 g/L)	0	45%
and Class F fly ash (w/c = 5)	5	35%
DBS (0.5 g/L)	0	50%
and Class F fly ash (w/c = 5)	5	35%
OL (0.5 g/L)	0	25%
and Class C fly ash (w/c = 5)	5	20%
DBS (0.5 g/L)	0	80%
and Class C fly ash (w/c = 5)	5	45%
OL (0.5 g/L)	0	10%
and $CaCl_2$ (1 g/L)	5	10%
DBS (0.5 g/L)	0	50%
and $CaCl_2$ (1 g/L)	5	40%

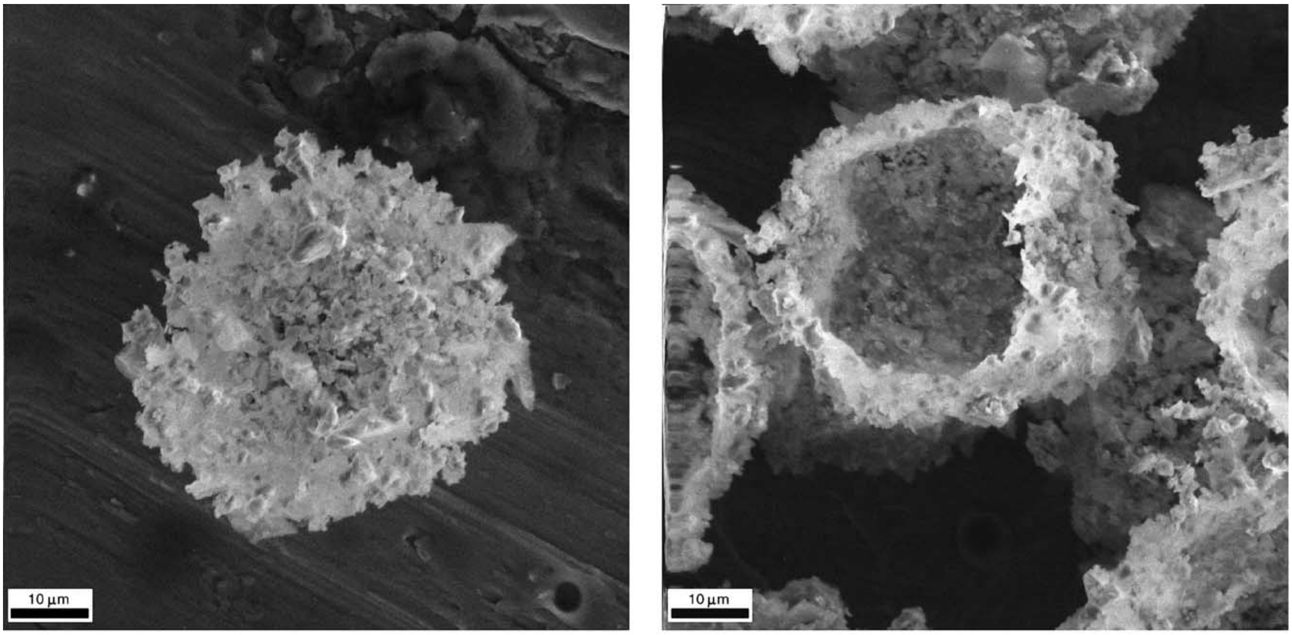
3.2.1. Glycerol method

This method was developed during this study as a means of isolating air bubbles from fresh cement paste, in the hope that they would retain some of their initial microstructure.

- A small amount of fresh cement paste is placed at the bottom of a test tube.
- A 5-cm layer of pure glycerol is poured over the cement paste, followed by a 5-cm layer of deionized water.
- The cement paste is slowly mixed by hand with a narrow glass stirrer to allow the bubbles to escape.
- The glycerol acts as a barrier between the cement paste and the water, through which the air bubbles can float without dilution of the paste by the water.
- The bubbles float through the glycerol and through the water, collecting on the top surface. They are often stable enough to be removed by scooping them onto a titanium plate, which is immediately mounted onto the specimen holder, quenched in liquid nitrogen and then imaged in the LTSEM.
- Unless otherwise noted, all pastes are quenched less than 30 min after mixing.

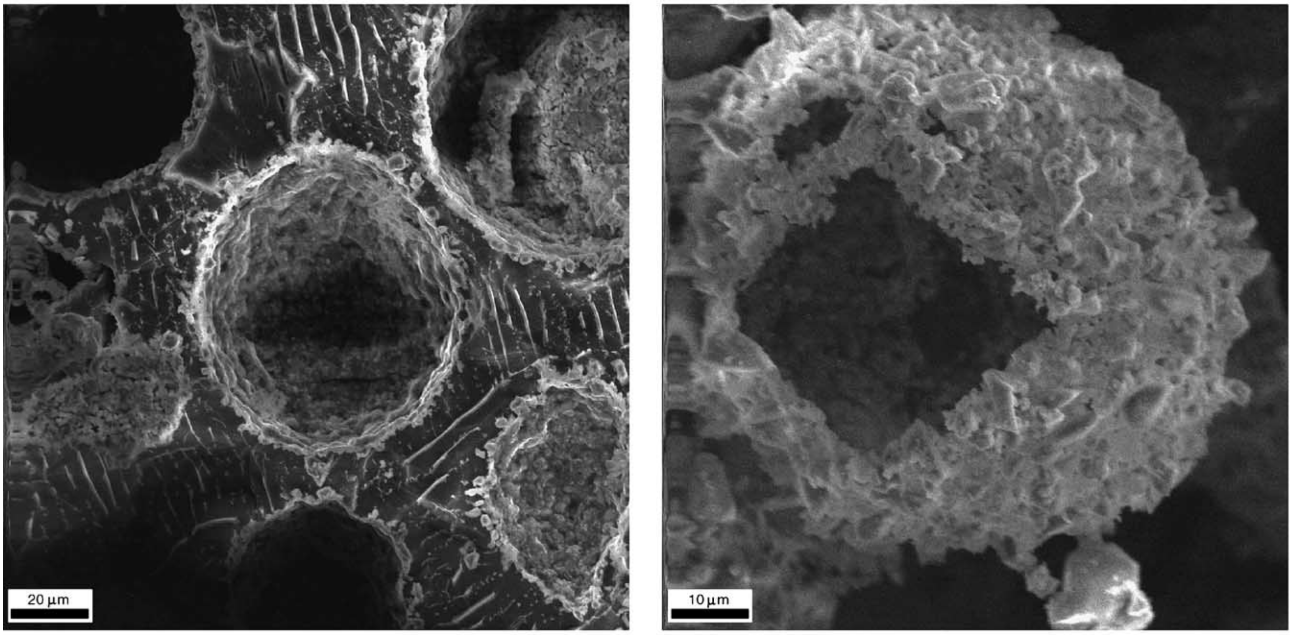
3.2.2. Fresh cement paste specimens

Fresh cement paste specimens can also be prepared for viewing in the LTSEM. For these experiments, specimens are mixed for 5 min and cast into a plexiglass mold. The entire mold is then quenched in liquid nitrogen. The mold is disassembled while still immersed in liquid nitrogen, and the specimen extracted. The result of the quenching is that



a. Generated with Cement Paste (w/c= 0.4) and Na Oleate as the AEA (after sublimation)

b. Generated with Cement Paste (w/c= 0.4) and Na Oleate as the AEA (after sublimation)



c. Generated with Cement Paste (w/c = 0.4) and Na DBS as the AEA (before sublimation)

d. Generated with Cement Paste (w/c = 0.4) and Na DBS as the AEA (after sublimation)

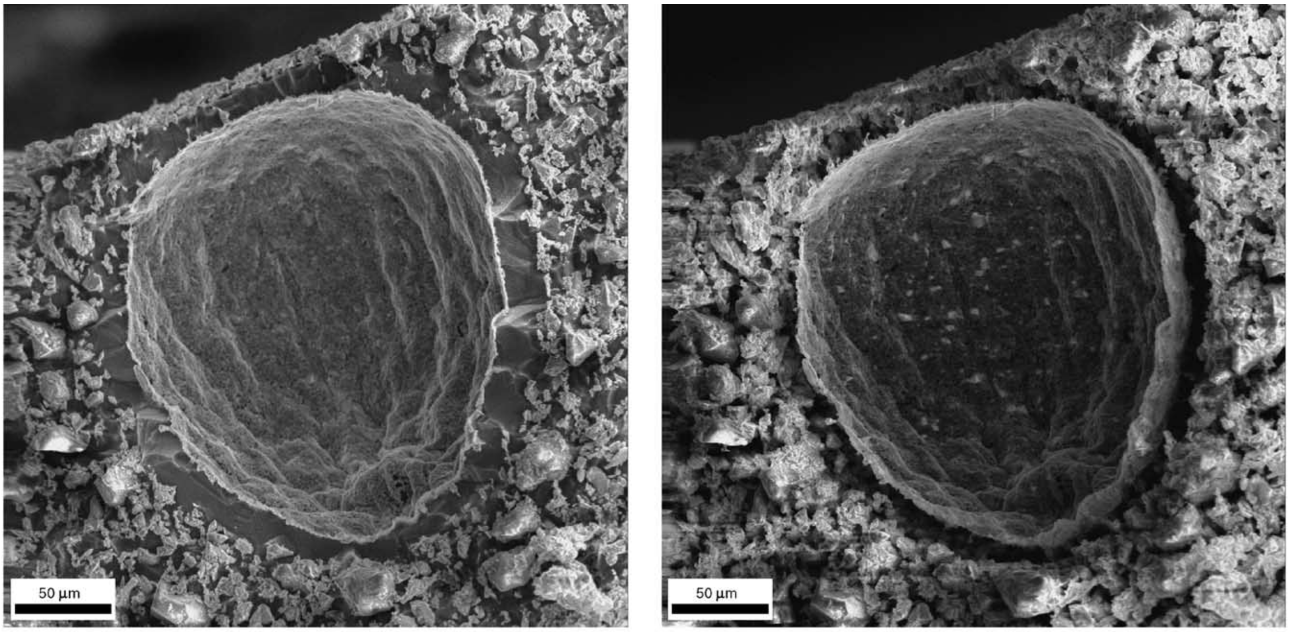
Fig. 1. Glycerol method specimens.

the specimen freezes quickly, reaching − 190 °C in approximately 10 s. Under these conditions, water forms hexagonal ice that appears homogeneous or "glassy" [8]. Thus, cement grains and air voids are "frozen" at their 5-min hydration states, and can be viewed in the LTSEM in their original orientation during early hydration.

4. Results and discussion

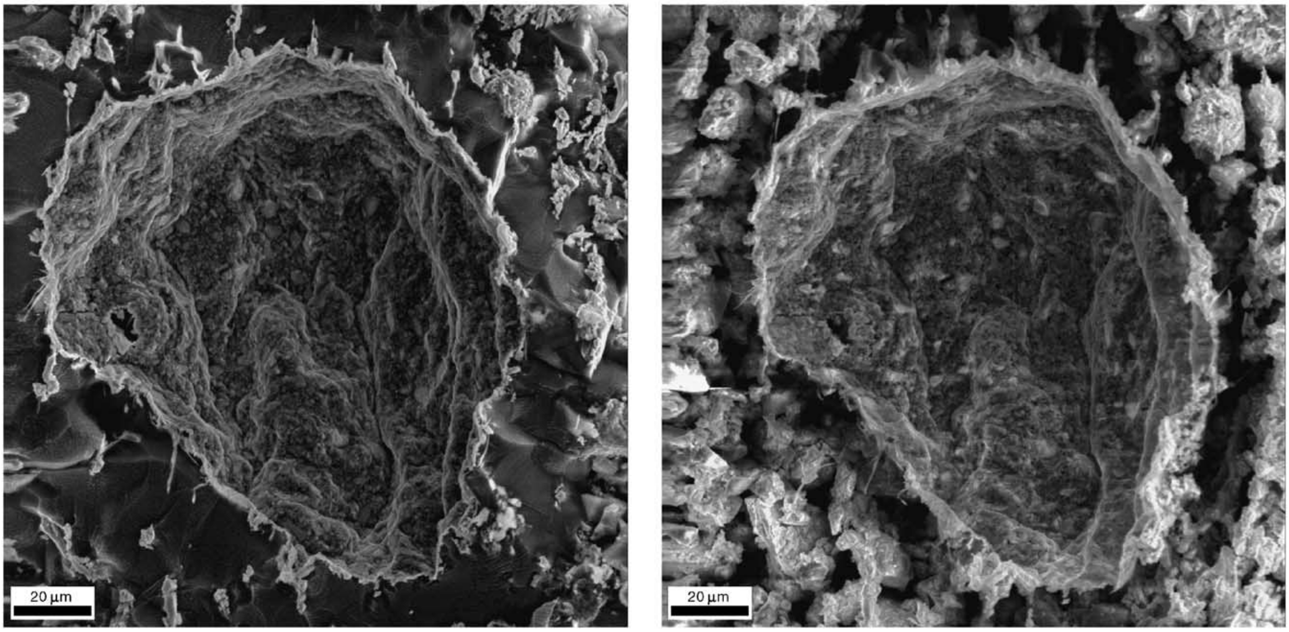
4.1. Foam index tests

The results of the modified foam index test are summarized in Table 2. As can be seen, the foams generated with sodium oleate in the presence of cement or fly ash tend to be slightly lower in initial volume than do the sodium DBS foams, but remain more stable. This result is consistent with previous data demonstrating the relative stability of the air void system generated with sodium oleate. The presence of portland cement or fly ash reduces the volume of foam relative to the system without suspended solids, indicating either adsorption of the surfactant by the solids or an inhibiting effect of calcium ions released by the cement. The effect is always slightly greater with the oleate than with the DBS. The contribution of calcium ions to this effect is evidenced by two additional tests with dilute calcium chloride solution, shown at the bottom of the table. From these results, it is clearly demonstrated that calcium ions in solution strongly inhibit the foaming of sodium oleate solutions, but have a much less severe effect on sodium DBS.



a. Cement Paste (w/c = 0.4), before sublimation

b. Cement Paste (w/c = 0.4), after sublimation



c. Cement Paste (w/c = 0.4), before sublimation

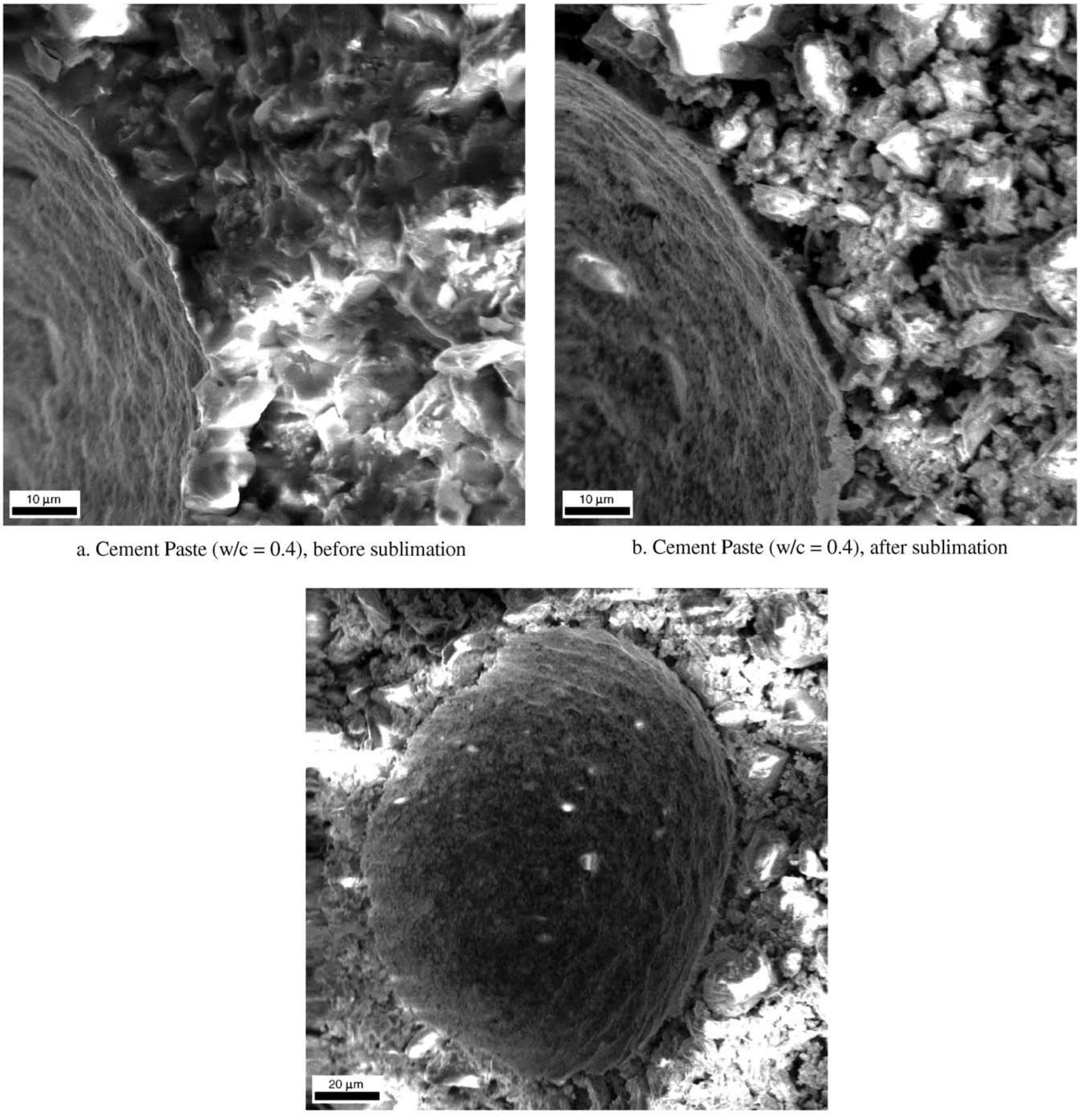
d. Cement Paste (w/c = 0.4), after sublimation

Fig. 2. Sodium oleate 5-minute specimens.

4.2. Low-temperature scanning electron microscopy

4.2.1. Glycerol method specimens

The glycerol method is used to extract bubbles from cement pastes mixed with AEAs, and Fig. 1 shows LTSEM micrographs of typical air bubbles recuperated using this method. Fig. 1a and b is from a cement paste made with sodium oleate. Fig. 1a shows the outside of a single bubble from the recuperated floating foam after sublimation of the residual water at -40 °C, and Fig. 1b shows a similar bubble that has been cut open with the cryochamber knife. These specimens retain their structure even on warming up to room temperature, indicating that the structure is essentially water-free after sublimation. The bubbles in Fig. 1c and d are similar but obtained from a paste made with sodium DBS. Note that Fig. 1c shows a section through a



a. Cement Paste (w/c = 0.4), before sublimation

b. Cement Paste (w/c = 0.4), after sublimation

c. Cement Paste (w/c = 0.4), after sublimation

Fig. 3. Sodium dodecyl benzene sulfonate 5-minute specimens.

frozen recuperated foam which has not been sublimed, and the particles surrounding the voids are clearly visible even under these conditions. In all cases, the air bubbles show the distinct shell that must have formed very early in the hydration process (after less than 30 min), and remained intact during specimen preparation. Shells around air voids have previously been observed in hardened concretes, by scanning electron microscopy [3,4], but the bubbles themselves have never previously been isolated from a fresh paste or concrete. The liquid-nitrogen quenched bubbles observed here are about 30–70 μm in diameter, and the shells appear to be made up of heterogeneous fine particles, 1–5 μm in size. (It should be noted that the quenched bubbles are almost certainly smaller than the original bubbles in the paste, because they would be expected to shrink to some extent during the liquid nitrogen quenching process.) It is possible that the shell is initially composed of precipitates that form a result of a reaction between the water-soluble part of the surfactant molecules and the cations (presumably, calcium) in the cement paste solution. However, the large size of the shell particles suggests that they are probably in part composed of fine cement particles that are carried up with the bubble on its passage through the liquid media (glycerol and water). The variation in size, irregularity and, nonuniformity of orientation of these particles is more consistent with collections of preformed particles. Any shrinking of the bubble during cooling would also tend to increase the area concentration of the solid particles on the bubble surface.

4.2.2. Fresh cement paste specimens

Fig. 2 shows micrographs from a fresh cement paste specimen made using sodium oleate as the air entrainer. Fig. 2a and c is taken while the specimen is still frozen, and Fig. 2b and d is the same location, respectively, after sublimation of water. As is seen in the glycerol method samples, the specimens show a shell around the air void that appears to be comprised of small particles or hydration products. The shell is easily identifiable in each location after sublimation. Also of interest is the appearance of a "transition zone" beyond the shell of each air void. The transition zone might at first sight be thought to be similar to the well-known transition zone frequently observed around aggregate particles in concrete [9], but, in this case, it may have been formed during quenching. The wrinkled appearance of the air void shell indicates that it may have occupied a larger space before quenching. Similar transition zones around air voids have been previously observed by LTSEM after 3 h of hydration [3,4]. The transition zone averages 10–15 μm thick for this specimen, and is characterized by a much higher porosity than the surrounding cement paste. Again, the transition zone is quite obvious in the postsublimation micrographs.

Fig. 3 shows micrographs from a fresh cement paste specimen made with sodium DBS. Fig. 3a is before sublimation, Fig. 3b is the same location after sublimation, and Fig. 3c is the entire void before and after sublimation. The air void shell is again readily apparent, especially in the postsublimation images. The air void shell appears to have the same morphology as was observed in the sodium oleate fresh specimen and the glycerol method specimens. The transition zone, however, is not nearly as thick in this specimen as it is in the sodium oleate-containing specimen.

5. Conclusions

1. Air voids have, for the first time, been isolated from fresh paste by a flotation method and then observed by cryomicroscopy. These bubbles show a mineral shell that is left behind after sublimation of all of the water. This shell appears similar to the shells observed in air voids in hardened paste or concrete specimens, or in early-age frozen pastes [1–4].
2. A transition zone between the air void and bulk cement paste of early-age specimens (5 min hydration) is often observable, especially when sodium oleate is used as the air entrainer. It is conceivable that the thickness of this transition zone is due in some degree to shrinkage of the air void during the liquid-nitrogen quenching process (before all of the water has frozen).
3. Calcium ions in the liquid phase reduce the effectiveness of air entrainment much more for sodium oleate than for sodium DBS.

Acknowledgments

The authors would like to thank Ms. Evelyn Clausnitzer of the Children's Hospital Oakland Research Institute for her assistance with the LTSEM analysis presented herein. We would also like to recognize the National Science Foundation (NSF grant 442408-21202) and the California Tobacco-Related Disease Research Program (grant 4RT-0832) for their continued support of this research.

References

[1] P.J.M. Monteiro, S.J. Bastacky, T.L. Hayes, Low-temperature scanning electron microscope analysis of the portland cement paste early hydration, Cem. Concr. Res. 15 (4) (1985) 687–693.

[2] P.J.M. Monteiro, A.I. Rashed, S.J. Bastacky, T.L. Hayes, Ice in cement paste as analyzed in the low-temperature scanning electron microscope, Cem. Concr. Res. 19 (2) (1989) 306–319.

[3] A.I. Rashed, R.B. Williamson, Microstructure of entrained air voids in concrete: Part I, J. Mater. Res. 6 (9) (1991) 2004–2012.

[4] A.I. Rashed, R.B. Williamson, Microstructure of entrained air voids in concrete: Part II, J. Mater. Res. 6 (11) (1991) 2474–2483.

[5] N.S. Tarasova, M.A. Khachaturyan, L.A. Nikolaev, Effect of low-frequency mechanical vibrations on solutions of surface active substances, Russ. J. Phys. Chem. 58 (4) (1984) 628–629.

[6] J. Pawley, J. Norton, A chamber attached to the SEM for fracturing

and coating frozen biological samples, J. Microsc. 112 (2) (1978) 169–182 (March).

[7] J. Bastacky, G.R. Hook, G.L. Finch, J. Goerke, T.L. Hayes, Low-temperature scanning electron microscopy of frozen hydrated mouse lung, Scanning 9 (1987) 57–70.

[8] P. Echlin, Lecture Notes, Joint Meeting of Delta Microscopy Society and Northern California Microscopy Society, January 17–18, 2001.

[9] P.K. Mehta, P.J.M. Monteiro, Concrete: Microstructure, Properties and Materials, Prentice Hall, New York, 1993.