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Cement and Concrete Research 33 (2003) 1531–1537

CEMENT AND CONCRETE RESEARCH

Observations of ice lens formation and frost heave in young Portland cement paste

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Received 23 May 2001; accepted 24 March 2003

Abstract

As part of a research program to image frozen cement past specimens, abnormal microstructural formations are seen in specimens frozen after 10-h hydration. The formations are areas of loose microstructure with aspect ratios of 6–10, which appear perpendicular to the direction of cooling in the specimen. After sublimation of the water in the specimens during the imaging process, these formations collapse, indicating that ice is instrumental to their structure. These formations coincide with longitudinal cracks in the specimen, which do not appear to be due to specimen preparation and are consistent with an internal tensile strain. The authors have hypothesized that ice lens formation and frost heave, or a similar freezing mechanism, is responsible for these microstructural features, which are seen in 10-h specimens and are absent in all other cement paste specimens. Triaxial permeability tests have also shown that the cement paste mix used in this study has a permeability at 10-h age of $\sim 10^{-6}$ cm/s. This permeability is similar to that of silty soil, some of the most susceptible to frost heave.
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Keywords: Freezing and thawing; Microstructure; Permeability; SEM; Frost heave

1. Introduction

Research recently completed at the University of California at Berkeley involves an experimental testing program to determine the microstructural characteristics of the entrained air voids of hydrated cement paste and the ice that forms in them in freezing conditions [1,2]. In this testing program, specimens are analyzed with a low-temperature scanning electron microscope (LTSEM), which allows for imaging of specimens in a frozen hydrated state. The cement paste specimens analyzed in this research program experienced varying moist hydration times and freeze–thaw histories.

In the present paper, microstructural formations specific to specimens imaged after 10-h moist hydration and 24-h freezing at -7 °C are examined. These formations are structurally similar to ice lenses, the central feature of frost heave in soils. The permeability and heat conduction processes that govern ice lens formation and frost heave in soils are complex. These processes require a distinct set of criteria necessary for frost heave. This paper will examine these processes and criteria and make comparisons between frost susceptible soil and cement paste specimens in this study. The result is the authors' interpretation of the mechanisms that caused the formations seen in the 10-h frozen cement paste specimens.

2. Theoretical background

Ice lens formation and frost heave are responsible for millions of dollars of damage in cold regions every year [3]. Ice lenses form parallel to one another at increasing depths in soil, heaving the soil mass to make room for themselves. The ice lenses generally result in a volume increase much greater than the 9% volume increase associated with the phase transition of water to ice. Soils can heave as much as 2 ft when the conditions are ideal. The heaving forces are amazingly large and can easily damage foundations, pavements and sidewalks [4,5].

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doi:10.1016/S0008-8846(03)00103-0

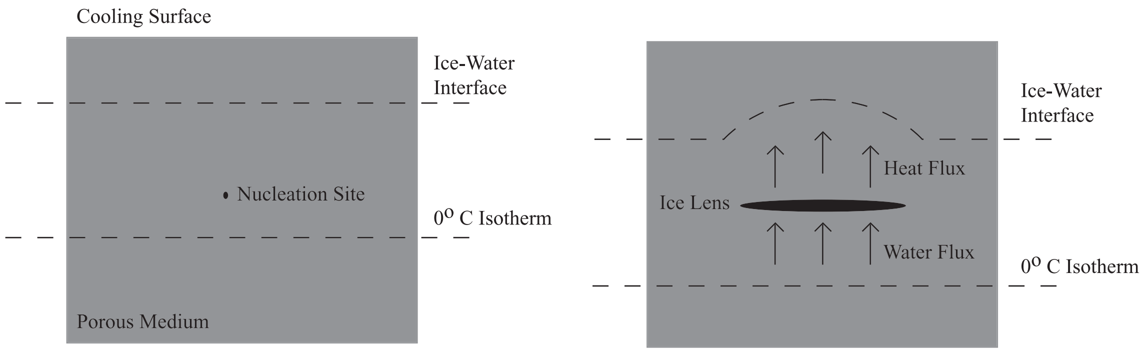

Fig. 1. Schematic of ice lens formation.

Ice lenses form through a complex interaction of mass and heat transfer. A schematic of ice lens formation is given in Fig. 1. A given porous material, cooled from one surface, will have a temperature at which ice and water are at equilibrium [4]. This temperature is generally lower than the equilibrium freezing point of free water due to the capillary and solute effects that depress the freezing point of water [6,7]. Thus, in a specimen cooled from one surface, the 0° isotherm will proceed ahead of the ice–water interface, where ice is forming spontaneously in all pores [5]. This effect creates a zone of undercooled water, behind the 0° isotherm but ahead of the freezing front. In this undercooled zone, there may be isolated pores large enough to allow nucleation to occur without general ice formation, as seen in Fig. 1. The presence of such a location is critical to the formation of ice lenses; without it, solidification will pass relatively evenly through the medium as the ice–water equilibrium isotherm passes.

If nucleation has occurred in a pore ahead of the freezing front, certain conditions must exist so that an ice lens can grow. Growth of this ice lens requires a steady supply of water. This supply appears in the form of supercooled water in the surrounding smaller, unfrozen pores, depicted as the "water flux" in Fig. 1. Water in the surrounding undercooled pores migrates towards the freezing site and crystallizes; the rate at which this happens depends on the permeability of the medium. This solidifying water releases its latent heat of fusion. Some of this energy is used as work to "heave" the soil mass to create space for the ice lens, and some energy is released as heat. This heat, depicted as heat flux in Fig. 1, is dissipated in the direction of the cooling gradient, which is towards the surface of the heaving medium. This heat raises the temperature near the freezing front and prevents it from progressing further into the medium. As the freezing front stalls, the ice lens continues to grow by draining the nearby undercooled pores. As long as the supply of water is large enough to suppress the progression of the freezing front, the ice lens will continue to grow.

At some point, water will not be supplied to the growing ice lens at a fast enough rate to keep the freezing front at bay. The freezing front will continue to progress deeper and will eventually engulf the ice lens. At this point, ice lens growth is terminated. The ice lens will remain, stabilized by the surrounding freezing temperature, but will no longer grow. If the conditions are still favorable, the process can repeat itself, and a new ice lens develops below the original one.

3. Experimental materials and procedures

The material studied in the paper is air entrained Portland cement paste. The cement is a standard ASTM Type I Portland cement, and its composition is summarized in Table 1. Deionized water is used as the mix water. The air entraining admixture (AEA) used in this study is a commercially available product that fully complies with standard specifications for AEA (ASTM Designation C260). The active component of the AEA is a saponified rosin, with characteristics similar to vinsol resin [8].

The mix design used for the cement paste specimens is given in Table 2. The AEA is diluted in the mixing water, then added to the cement and mixed for 5 min. For the specimens in this study, the cement paste is cast into Plexiglas molds ($8 \times 7 \times 2$ mm), covered with plastic wrap and cured in a fog room (100% relative humidity) for 10 h. After demolding, the specimens are wrapped in several layers of plastic and aluminum foil and frozen at -7 °C for 24 h.

Table 1
Cement characteristics (mass %)

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

Table 2
Mix design

Material	Mass (g)
Water	160.0
Type I cement	454.5
AEA	30.0

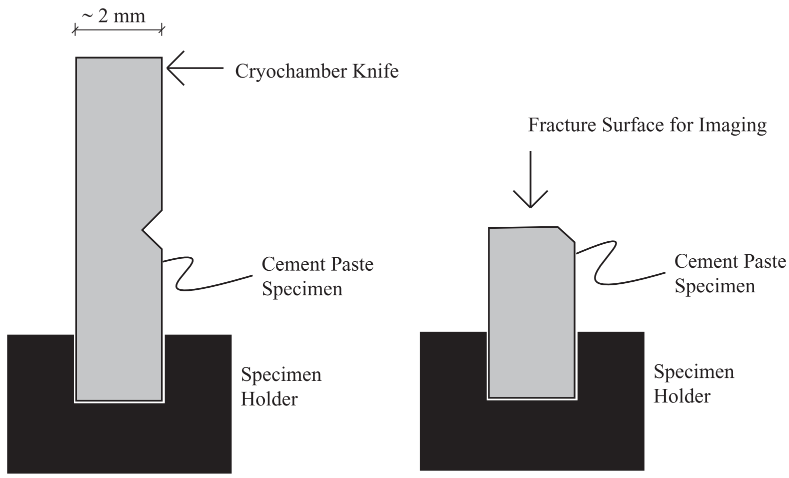

Fig. 2. Fracture procedure in LTSEM cryochamber.

Following this freezing period, the specimens are quenched in liquid nitrogen and prepared for imaging in the LTSEM. The LTSEM allows specimens to be imaged at very low temperatures (− 190 °C). At this temperature, the vapor pressure of water is so low ($\sim 10^{-10}$ torr) that very little water sublimes from the surface of the specimen. The LTSEM is also fitted with a multipurpose specimen preparation "cryochamber," which keeps the specimen at liquid nitrogen temperature during preparation. The cryochamber is fitted with a knife that can be used to fracture the specimen, as depicted in Fig. 2. This fracture process allows for the imaging of the interior of a frozen hydrated specimen. The LTSEM images presented here will be of the imaging surface depicted in Fig. 2, which is ~ 1 mm wide and 8 mm long. Specimens can also be warmed in the LTSEM chamber, which allows the surface ice of the specimen to slowly sublime. Starting from the running temperature of − 190 °C, the sublimation of all surface ice in the specimen takes ~ 15 min. More details on the LTSEM and its applications in cement paste research are available in the literature [1,2,9,10].

The triaxial permeability test is used to determine the permeability of cement paste at this 10-h age. The triaxial test involves generating a pressure gradient across a representative section of the medium of interest and recording the flow rate through the specimen. The flow rate and pressure gradient are used in conjunction with Darcy's law to deter-

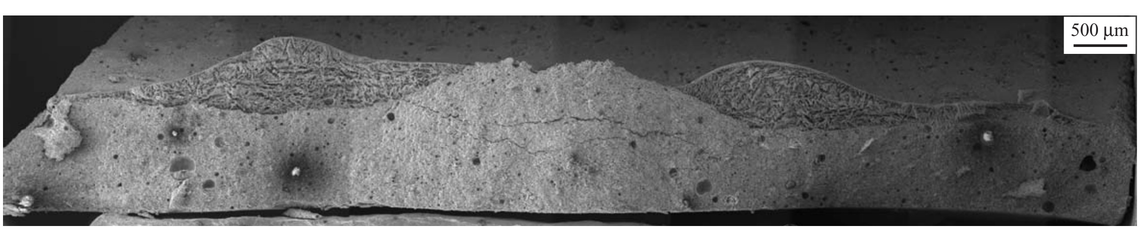

Fig. 3. Specimen CPA, before sublimation.

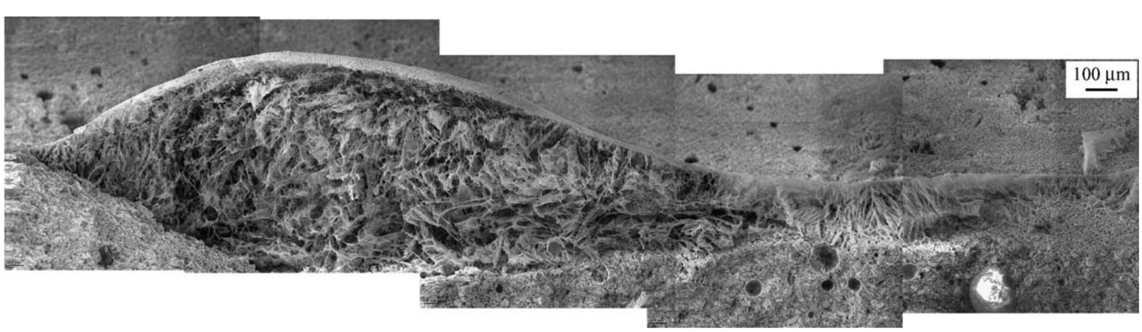

Fig. 4. Specimen CPA, right side formation from Fig. 3, before sublimation.

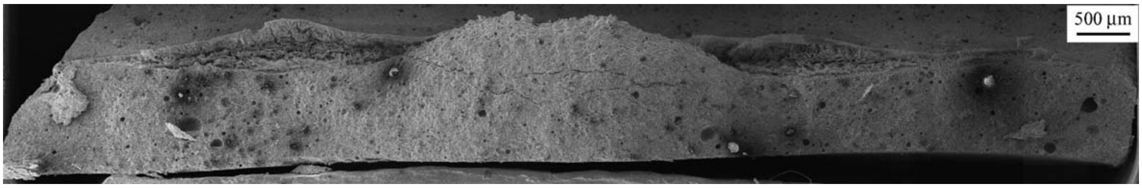

Fig. 5. Specimen CPA, after sublimation.

mine the hydraulic conductivity or permeability of the specimen.

4. Observations

The first specimen considered is specimen CPA. A composite micrograph of the entire specimen CPA is given in Fig. 3. The first significant features to note in Fig. 3 are the two large formations at the top of the specimen. Formations of this type are only observed in specimens cured for 10 h prior to freezing at -7 °C; younger and older specimens did not show evidence of these formations [1,2]. A high magnification image of the right side formation is given in Fig. 4. The microstructure of the formation is very loose, with interconnecting fibers throughout the formation. Fig. 5 shows the entire specimen after sublimation; both of the formations near the top of the specimen have collapsed. Fig. 6 shows the same formation as Fig. 4 after sublimation of the ice in the specimen. The structure has collapsed on itself, which indicates that there is some ice in the formation in Fig. 4. Apparently, the ice helps to support the structure in some way, and in its absence, the formation collapses.

Returning now to Fig. 3, note the longitudinal cracks near the center of the specimen. These cracks are in a plane orthogonal to the plane of fracture in the cryochamber (Fig. 2), which implies that they are not related to the fracture of the specimen. Cracks of this type are not seen in any younger or older specimens [1,2]. Since it is unlikely that cracks of this type are due to the specimen preparation, the cracks probably occur sometime during the specimen's freezing.

The second specimen to be considered is specimen CPB, which is identical to CPA in mix design, curing conditions and age at freezing. A composite micrograph of the entire specimen CPB is given in Fig. 7. Again, a large formation is readily apparent, this time deeper in the specimen. A high

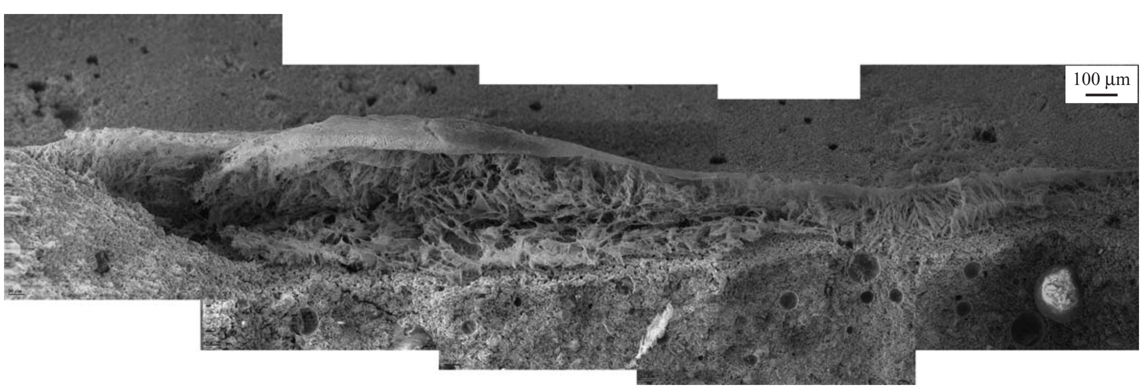

Fig. 6. Specimen CPA, right side formation from Fig. 5, after sublimation.

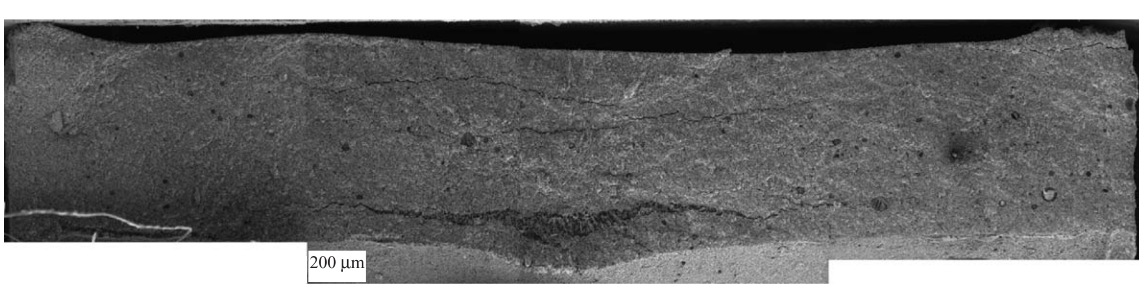

Fig. 7. Specimen CPB, before sublimation.

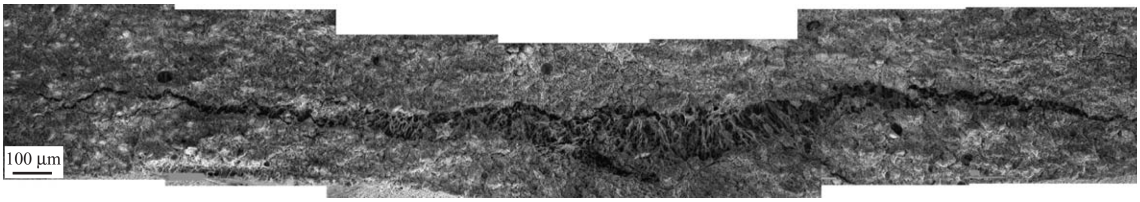

Fig. 8. Specimen CPB, formation from Fig. 7, before sublimation.

magnification image of the formation is given in Fig. 8. The same loose microstructure seen in Fig. 4 is also apparent in Fig. 8. Figs. 9 and 10 show the entire specimen and formation, respectively, after sublimation. Although some microstructural changes are apparent in these postsublimation figures, the entire structure seen in Fig. 8 does not collapse as the formations in specimen CPA did. This does not necessarily mean that ice is not present in the formation in Fig. 8; only that if present, it is not critical to the stability of the formation. The longitudinal cracks seen in specimen CPA also appear in specimen CPB. For both samples, ice was not observed in air voids.

It appears that the same mechanism is at work in both specimens. The microstructure of the formations in the two cases is quite similar. Both formations have aspect ratios of ~6–10, occur parallel to the main axis of the specimen and are aligned perpendicular to the direction of cooling in the specimen. Also apparent in both specimens are longitudinal cracks that are not likely to have been caused by the fracturing process of specimen preparation. These cracks are consistent with a heaving process from within the specimen. It is therefore hypothesized that a mechanism similar to frost heave and ice lens formation and soils is responsible for the observations outlined here for cement paste at 10-h age.

5. Analysis and discussion

Mitchell [3] outlines three conditions necessary for a favorable ice lens growth environment:

1. a frost susceptible medium,
2. a freezing temperature and
3. a supply of water.

Criterion 2 is clearly met, with the temperature in the freezing chamber at -7 °C. For a saturated medium, as is the case for the cement paste specimens cured at 100% relative humidity, criterion 3 is directly related to the properties of the medium and is therefore linked to criterion 1. Support of the hypothesis that the formations in Figs. 3–

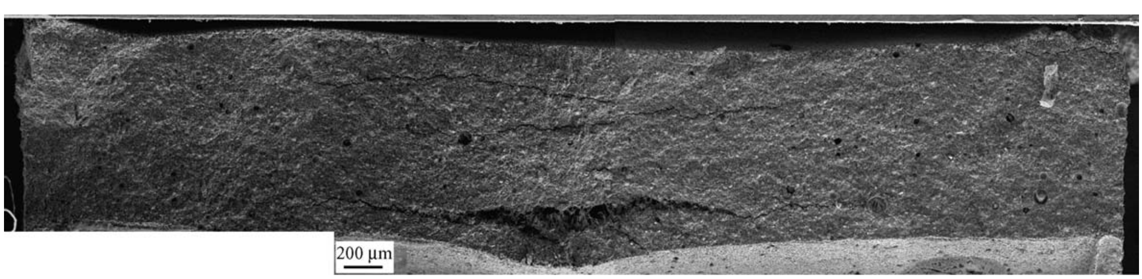

Fig. 9. Specimen CPB, after sublimation.

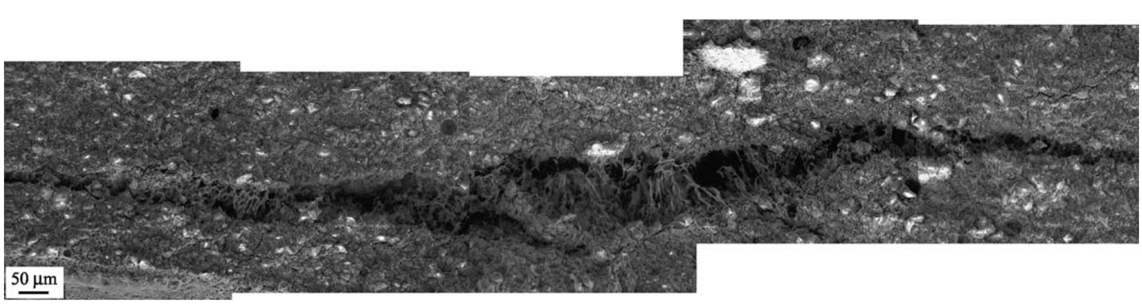

Fig. 10. Specimen CPB, formation from Fig. 9, after sublimation.

10 are indeed results of frost heave or similar events will therefore center on the confirmation of criterion 1 with respect to cement paste at 10-h age.

Criterion 1 requires a frost susceptible medium for ice lens formation and growth. The theoretical background section demonstrates that for ice lens formation, the medium must be dense enough to hinder general ice formation but porous enough to allow sufficient water flow. Both of these requirements of a medium such as cement paste are directly related to the permeability of the medium.

A triaxial permeability test has been run on the cement paste mix design given in Table 2. The permeability specimen is cast into a standard 3×6 in. cylinder and cured for 9 h. Because the permeability test is a time-dependent process, the cylinder is tested from 9 to 11 h of age, with the result being used as an estimate for the permeability at 10 h. The permeability test results give an average hydraulic conductivity of 10^{-6} cm/s for this cement paste mix design at 10 h, which is comparable to the permeability of a silty soil. This type of soil is one of the most susceptible to frost heave [3]. Data from triaxial permeability tests on cement paste at other ages are not available. At younger ages, the test is dominated by the high rate of hydration occurring inside the specimen, while at later ages, the water throughput is so low that extremely high pressures are required to cause a measurable flow. These high pressures can cause edge effects in the specimen as well as nonlinear flow, both of which render the results inaccurate for Darcy's flow. Qualitatively, however, it must be expected that at some point during the evolution of a cement paste specimen, the permeability would drop to a level where the specimen would be susceptible to frost heave. This triaxial test result demonstrates that at 10-h age, the permeability is similar to a soil susceptible to frost heave. In the absence of this permeability data, it must also be noted that most porous media can be made to heave, pending the proper conditions during freezing [7].

It is important to note the differences between the specimens in Figs. 3–10 and the soils that are typically observed to frost heave in the field. In the field, one restriction to ice lens formation is the overburden pressure; the mass of ice and soil above the forming lens must be lifted in order for the lens to grow. Due to the small size of the specimens in this study, this resistance is negligible. Secondly, the specimens are cement paste, and at 10-h age, the mechanical and permeability characteristics of the cement paste specimens are changing rapidly. At earlier ages, the pore structure is probably too loose to prevent ice formation coinciding with the 0° isotherm. At later ages, the tensile strength will be sufficiently high to prevent significant growth of ice crystals beyond the pore in which they nucleate. Another important point is the relatively severe freezing process the specimens undergo: these specimens freeze much more rapidly than soils in the field, where temperatures typically drop by only a few degrees per hour. With these differences in mind, the hypothesis that frost heave, or a similar mechanism, is causing the formations in Figs. 3–10 is remains viable. This is because of the absence of such formations in all other specimens [1,2] and the permeability and mechanical properties of cement paste at 10-h age. Further experimental and theoretical study of cement paste microstructure at this age is necessary to determine the exact mechanism and its relation to frost heave.

There are a number of significant implications to these observations in young cement paste. First, these results highlight the inherent risk in allowing cement paste and concrete to freeze at young ages. It has long been known that allowing fresh cement paste to freeze results in significant damage, but this belief is based solely on the high freezable water content and lack of tensile strength in the fresh cement paste. Here, it has been shown that significantly more damage than the simple 9% volume increase in the transition from water to ice is possible if freezing occurs in fresh cement paste. The large cracks seen in the specimens would certainly compromise the mechanical integrity of structural systems in service. These cracks could also hasten the onset of other durability concerns such as reinforcement corrosion and sulfate attack [11].

The results presented here also give insight to the microstructure of cement paste at this age. Because of the small dimensions (about 2 mm perpendicular to the plane of frost heave) of the LTSEM specimens described here, it is likely that they freeze rather quickly in the − 7 °C chamber. A nucleation must occur ahead of the general freezing front for an ice lens to form, and nucleation is a statistical process [12]. The more elapsed time and potential nucleation sites, the higher the likelihood that a nucleation will occur. Since the specimen is so small and freezes quickly, favorable nucleation sites that can result in ice lens formation and growth are probably abundant in cement paste at this age. It is unlikely that these nucleation sites are young capillary pores, since this scenario would cause the general freezing front to coincide with the 0° C isotherm, which makes ice lens formation impossible.

6. Conclusions

Formations that are microstructurally similar to ice lens formation and frost heave in soils have been observed with the LTSEM in air entrained Portland cement paste at 10-h age. Also apparent in the frozen specimens at this age are longitudinal cracks that probably occur as a result of tensile strains from within the specimen. Theoretical consideration and permeability tests indicate that, at this age, cement paste could be susceptible to ice lens formation and frost heave or similar freezing mechanisms.

Acknowledgements

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 here. 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.

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