

Study of Cement Paste Setting at Microstructural Level

by G. Venkiteela and Z. Sun

Synopsis: In this study, various fresh cement paste microstructure evolutions were observed during setting in a conventional SEM by employing a new sample technique called Quantomix capsuling system. Individual cement particle and different phases growths were studied quantitatively by using image analysis techniques on observed micrographs. The ASTM C191 method was used to determine the cement pastes setting times and further the developments of different phases in the cement pastes microstructure were studied at various stages of setting. It was observed that irrespective of the water to cement (w/c) ratio, cement particle connectivity plays a major role in Vicat needle settlement (or in cement paste setting); however, it was observed that w/c ratio influences the hydration rate in mixtures. It was also observed that during setting water phase depletion wholly depends on richness of the mixture, whereas solid phase growth is a combined effect of cement particle growth and connectivity.

Keywords: cement paste; scanning electron microscopy; setting.

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INTRODUCTION

Concrete setting is a complex phenomenon, which is governed by the evolution of microstructure in its cement paste. The evolution of cement paste's microstructure includes a series of chemical reactions and physical changes in its cement particles. In cement paste, hydration happens as soon as water is mixed with cement powder, during this period, cement particle dissolution, precipitation, agglomeration, diffusion and variety of other reactions occur simultaneously.¹ But it is still unclear how these developments in cement particles influence the cement paste microstructure evolution during setting. In construction field concrete setting time is also an important parameter in deciding the scheduling of different events, because remixing, replacing or altering the original concrete mass cannot be possible once concrete sets.

Cement pastes setting behaviors can be determined by using various methods, such as Vicat needle method,² ultrasonic wave method,³ and electric resistivity method.⁴ All these methods define setting time with the help of a particular material property at macro level. However, these methods fail to give direct information on cement paste microstructure evolution during setting. For better understanding of cement paste setting using these methods, a combined study is required between these methods and to that of other methods which will give insight information on cement paste microstructure developments. Researchers are using imaging methods such as neutron scanning,⁵ soft X-ray,⁶ X-ray microtomography⁷ and scanning electron microscopy⁸ (SEM) to observe the developments in microstructures of cement-based materials. Among these methods SEM has been used widely to study the microstructure of cement pastes in hardened concrete,⁹ the hydration process of cement pastes¹⁰ and the mineralogy of clinker and cement powder.¹¹ All the SEM experiments require samples in harden state along with sample preparation processes like drying, freezing, resin coatings etc. Although environmental SEM (ESEM) is suitable for wet samples, ambient temperature changes in chamber limit the usage in wet cement pastes.

A new in-situ technique was proposed¹² for fresh cement-based materials. Using this technique, wet samples can be placed directly in a capsuling system and corresponding micrographs were captured by using a conventional SEM. Katz et al.¹³ conducted preliminary studies on this technique to investigate the hydration of gypsum and cement. It was found that with the help of this capsule, the sample preparation was become very convenient. It was also reported that both CSH and CH have been seen around cement particles during hydration. Later, Gallucci and Scrivener¹⁴ investigated the potential use of these capsules for the hydration of Portland cement with and without admixtures and also hydration of alite. They also appreciated the ease of sample preparation process, and the capability of studying the hydration of cement based materials dynamically. Further details regarding effective way of using these capsules and limitations can be found in Reference 14.

The objective of this research is to study the setting behavior of various cement pastes at microstructural level and to compare the different phases (especially solid and water) growth during setting. For this purpose four different cement pastes were prepared with water to cement (w/c) ratio 0.38, 0.5, 0.6 and 0.7 and their corresponding microstructures and setting times were observed using a conventional SEM in association with a capsuling system and ASTM-C191 method, respectively. Using an image analysis tool, different cement particle growths and different phases growths were studied qualitatively and as well as quantitatively. Further the physical changes in different phases were compared at various stages of setting with the help of Vicat needle settlement readings.

RESEARCH SIGNIFICANCE

Preliminary in-situ studies were conducted on cement pastes setting behaviors at microstructural

level by employing a capsuling system in conventional scanning electron microscope (SEM). Using the SEM micrographs, which were taken continuously during cement paste setting, cement particle growth and solid and water phases evolutions were studied. An attempt was made to better understanding of ASTM C191 method by comparing the different phases developments during various cement pastes setting. The observations on physical changes in cement pastes microstructures can help to enhance knowledge on cement hydration kinetics and further improve the understanding of setting behaviors in concrete.

EXPERIMENTAL WORK

Material and testing conditions

Plain cement pastes with w/c ratios equal to 0.38, 0.5, 0.6 and 0.7 were prepared by using ordinary Type I portland cement and tap water. All the experiments were conducted at 23°C (73.4°F) and 100% humidity conditions.

SEM testing

Image capturing—A capsuling system was used in sample preparation process for the observation of fresh cement paste microstructure in conventional SEM as shown in Fig.1 (a). During the sample preparation process, cement powder was mixed with water by hand for about 3 to 4 minutes and transferred into the capsuling system to image in the SEM. Detail sample preparation process can be found in [14].

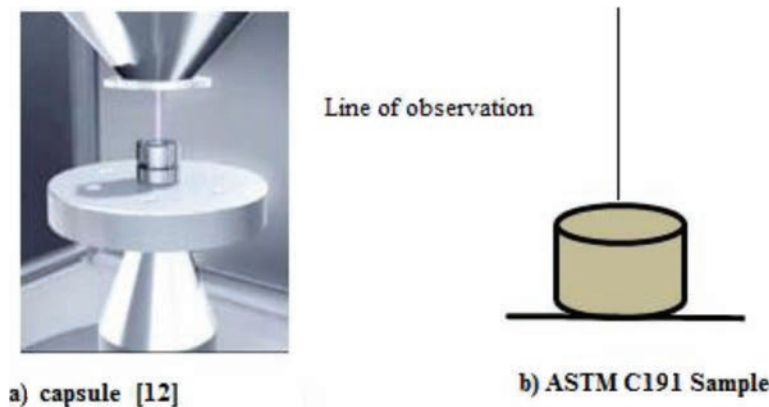


Fig. 1—Experimental samples.

All the SEM micrographs were captured by using back scattered electron (BSE) detector at magnification of 800X with observations being conducted at 20kV and working distance of 7.5 to 8.5 mm (0.3 to 0.33 in.). From this capsuling system, it is possible to have a continuous observation of cement paste micrographs for a particular region with the help of grid surface system on its membrane. All the four cement paste micrographs were captured up to 8 hours after mixing. Sample micrographs of cement paste (with w/c ratio 0.5) at various ages are as shown in Fig. 2 (a). For all the cement pastes, experiments were conducted in SEM with the same contrast, brightness, and chamber temperature. During the study three experiments for each w/c ratio were conducted along with observations of five grids in each experiment (capsule). Because of vertical observation on capsules membrane (Fig. 1 (a)), the formation of edge pits (surface undulations) were also observed on cement pastes surface, which can be observed in micrograph of cement paste in Fig.2 (a) at 6 hour age. The quantification process of changes in different phases and cement particle growth in these micrographs is explained in the following section.

Image analysis—The solid and water phases in SEM images were distinguished by using a threshold method¹⁵, which is based on the gray level histogram of SEM image. Using the histogram, binary segmentation was applied to pixels of a particular gray level (fixed) value of water (which is calibrated on SEM images at 15 min) and then area fractions of both phases (water and solids) in binary image were estimated by choosing areas represented in black or white color (Fig. 2 (b)). Having the difficulty in separation of gray levels for mixing water from that of cement particles in fresh cement pastes, various cement

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pastes SEM images at age 15-25 minutes were studied, and a gray value of 45 was fixed for initial water assuming that the majority of the water molecules are not contributed in hydration during this short period (that is, water is 45 or less and total solids are greater than 45 on a scale of 255). Figure 2(b) shows the binary segmentation of original micrographs (Fig. 2(a)) using threshold method, and features in black and white represent total solids and water respectively. By using this method all the captured micrographs area fractions (solid and water) were analyzed. It can be noted that all the measurements are in 2D; however, based on the Stereological principles,¹⁶ these 2D features can be approximately related to 3D elements of relative phases.^{17,18} Further, using threshold method, single particle growth was also quantified by choosing a desired particle in the original micrograph.

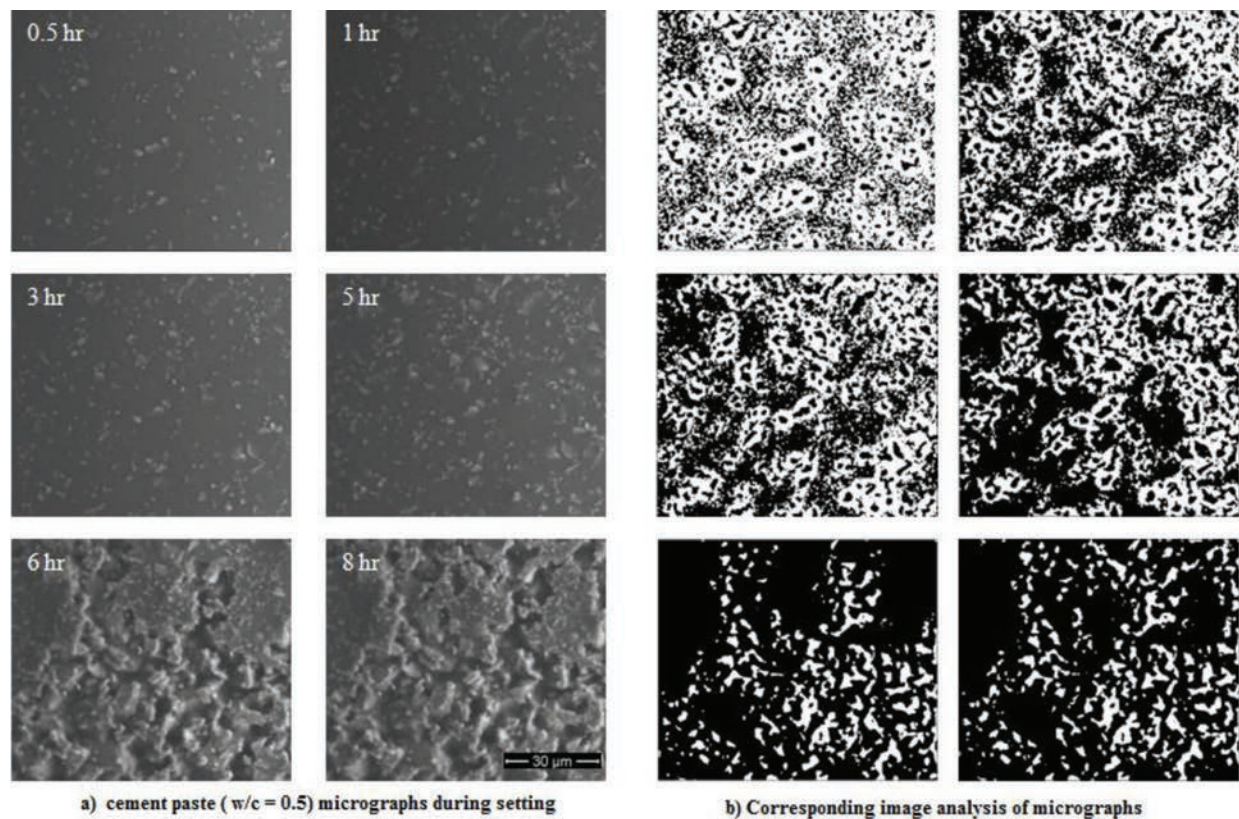


Fig. 2—Cement pastes SEM micrographs and image analysis.

Vicat needle method

Initial and final setting times of cement pastes (Fig. 1(b)) were determined by Vicat needle test as specified by ASTM Standard C191-08.¹⁹ An example of the measured displacement of the needle with time is given in Fig. 3. The mean values of the readings from the three batches were used to define the initial and final setting time of each plain paste mixture. The measured initial and final setting times for the pastes with w/c ratios changing from 0.38 to 0.7 at 23°C (73.4°F) are listed in Table 1.

Table 1—Cement pastes setting times

w/c	Initial setting time, hours	Final setting time, hours
0.38	4	6
0.5	4.8	7.15
0.6	5.30	8.50
0.7	6.15	9.30

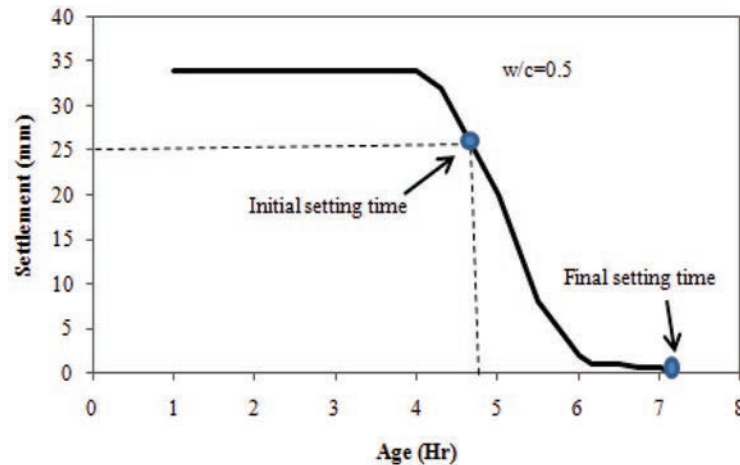


Fig. 3—Settlement of the needle during Vicat needle test. (Note: 1 mm = 0.03937 in.)

RESULTS AND DISCUSSIONS

Visual appearance of cement paste micrographs

Having the advantage of continuous observations of cement pastes micrographs in capsules right from the 30 minutes to final setting, it can be possible to observe the changes visually in SEM images. As shown in Fig. 2 (a), as the hydration is progressing, cement particle movements and texture changes can be seen in micrographs. The same changes can be also seen in corresponding binary images as shown in Fig. 2 (b). Particularly image analysis of original micrographs shows the change in density of black color (which represents solid) changing from low to high values as the fresh cement paste likely to be set. A sudden change in original micrographs texture has been observed after cement paste's initial setting, which may be indicating the arrival of steady state between the gray level values of different phases in cement pastes. It has also been observed that formation of surface undulation or edge pits in cement paste surface in between initial and final setting times of cement pastes (see Fig. 2 (a) at age 6 hours). All these visual changes in SEM images help to preliminary understanding of the nature of the microstructure evolution during setting.

Different sized particles growth

The change in individual cement particle diameter with time was measured to investigate the growth of cement particle in terms of Feret's diameter, which is defined as the longest possible distance between any two points along the selection of boundary¹⁶. Cement particles were classified in to three groups with the majority of particle diameter falling in the ranges of 2-5 μ m, 7-10 μ m, and 10-15 μ m. During the image analysis, a particle was selected from the initial micrograph and analyzed up to maximum age at which cement particles visually not appeared to be connected in respective micrographs of four cement pastes. A total of 30 particles in each size group were analyzed from all the four cement pastes, and the normalized average sizes and corresponding linear regressions of these particles are as shown in Fig. 4. Figure shows that 6 hours after mixing, particles with diameters of 2-5 μ m have increased about 25% compared to their original sizes, for the 7-10 μ m size group, the average diameter is increased by 20%, while for 10-15 μ m size group, particles are about 14% bigger than their original sizes. The reason for this high growth rates in smaller particles is the larger surface area to volume ratio, which helps to enhance their hydration rate¹. The linear regression also shows (Fig. 4), irrespective of w/c ratios, smaller particle's growth rate (slope of the linear regression line) is higher compare to larger particle's. However, due to the less surface orientation changes during the hydration process, 10-15 μ m group have steady growth rate (less scattered data points) among the three group particles.

Different phases developments during cement pastes setting

Solid phase—Fig. 5 shows the changes in area fractions of total solids and water in four cement pastes, and corresponding Vicat needle settlements at various ages. In figure, cement paste's initial and final

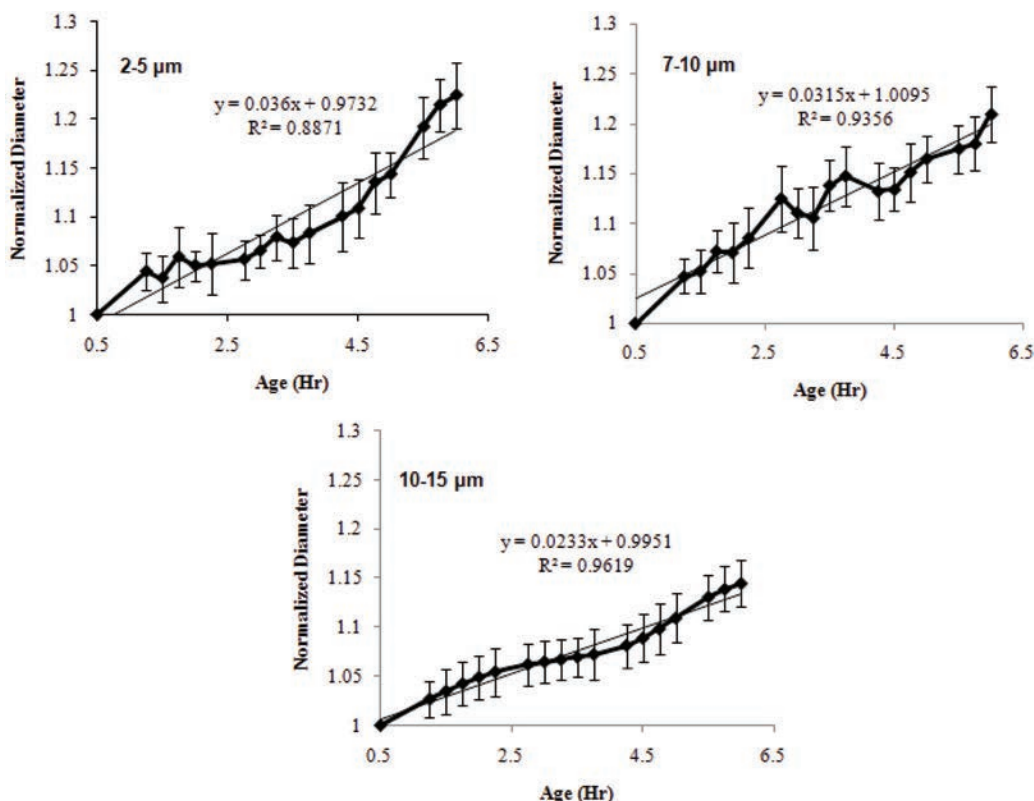


Fig. 4—Different sized particles growth.

setting times are identified by solid large and small dots respectively (here the area fractions are only approximation to the original volume fractions). The original area fraction of the solid phase in each cement paste before mixing (0 hr in Fig. 5) was calculated based on w/c ratio and the specific gravity of cement powder. Here the total solids area fraction includes CSH, CH crystals, unhydrated cement, chemically combined water and fine pores within the particles, which are not falling in the range of gray level value 45. It can be noticed that for all these four pastes, the water volume is reducing and the volume of solids is increasing as the hydration of cement paste progresses. It can be observed that initial setting for each paste is occurring at different times, for example, initial setting time of cement with w/c ratio 0.5 (4.8 hours) is larger than cement paste with w/c ratio 0.38 (4 hours). It is believed that needle settlement or resistant to needle penetration is not only depending on the amount of solid phase, but also depends on its structural arrangements within solid phase i.e. particle connectivity^{1,20} etc. Further in lower w/c ratio mixtures (high richness of the mixture), the cement particles and corresponding hydration products grow faster like a combined unit much earlier compared to higher w/c ratio mixtures, which seems to help in displaying the high resistance to needle penetration at early times. Authors also tried to study this effect of particle connectivity in terms of change in their gray level values before and after connectivity, but due to the limited scope of this paper these results are not discussed herein. At the time of final setting, it is observed that the surface of cement paste and as well as the amount of the both phases dramatically change. From the figure, it can be noticed that the area fractions of solid phase change from 45% to 85%, 38% to 82%, 35% to 77% and 30% to 72% for pastes with w/c ratio 0.38, 0.5, 0.6 and 0.7, respectively.

Water phase—Water is a critical phase, which decides the hydration rates and pore phases in cement pastes. As shown in Fig. 5, the amount of water is reducing as the hydration progress; but this reduction seems to be more in higher w/c ratio mixtures particularly at very early ages, which can be observed by the water phase depletion profiles of four cement pastes in Fig. 5. The main reason for this behavior seems to be the larger hydration rates in higher w/c ratio mixtures. It can be observed that approximately 50% reduction in water content is observed at initial setting time for mixture with w/c ratio 0.5,

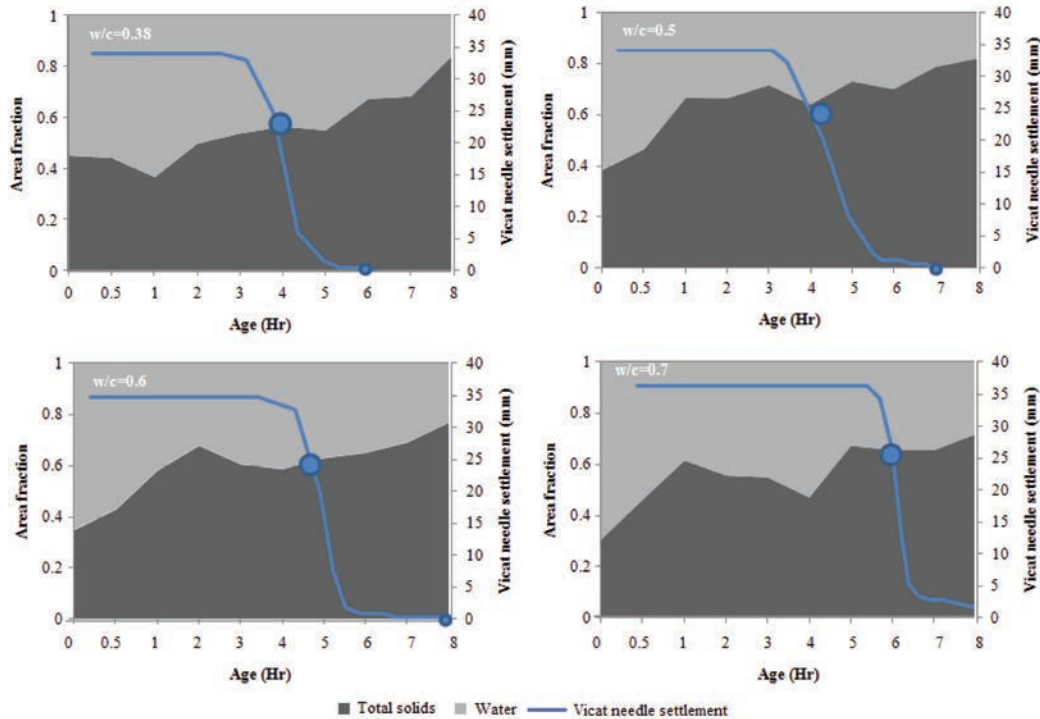


Fig. 5—Different phase developments during cement paste setting. (Note: 1 mm = 0.03937 in.)

0.6 and 0.7 compared to their initial value at beginning of mixing. However, in cement pastes with a w/c ratio of 0.38, this amount of reduction is occurring at longer times. This kind of behavior explains that in lower w/c ratio mixtures solid phase is dominating during initial set and moreover the consumption of water by cement particles totally depends on the cement particle population of the mixture.

CONCLUSIONS

From this study, following conclusions can be drawn:

1. Preliminary in-situ studies were conducted on four different cement pastes at microstructural level for better understanding of the cement pastes setting behaviors.
2. Capsuling system was used in SEM in-situ observation of fresh cement pastes, which drastically simplifies the sample preparation process of fresh cement pastes.
3. The developments in cement pastes micrographs during setting can be visually seen in original SEM micrographs and as well as in corresponding binary images.
4. Image analysis of different sized particles growth shows that on an average 20% increment in cement particle diameter is observed when they are in individual state during setting.
5. In lower w/c ratio mixtures cement particles speedy connectivity plays a major role in the early resistant to Vicat needle settlement compare to higher w/c ratio mixtures, however due to larger hydration rates, higher w/c ratio mixtures produces larger amount of area fraction of solids.
6. Water phase depletion profiles of higher w/c ratio mixtures shows that approximately 50% reduction in its original water content during initial setting. Whereas the same amount of water reduction appeared at longer ages for lower w/c ratio mixtures.
7. Further in-depth studies are required to understand the cement particle connectivity during setting and a better understanding of cement pastes setting behaviors can be possible by studying cement pastes setting at microstructural level.

ACKNOWLEDGEMENTS

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X-Ray Nanotomography of Cement Microstructure

by D. A. Lange, Y. Jia, and Y.-S. Liu

Synopsis: X-ray nanotomography was explored for investigation of the microstructure of cement paste in various ages, including 1-day and 28-day. 2D and 3D images were obtained for quantitative analysis and morphological reconstruction. The technique also provided a prospect of viewing interfacial transition zone (ITZ), of which the microstructures were simulated and the evolution of components with respect to the distance from the interface was calculated.

Keywords: interfacial transition zone (ITZ); microstructure; nanotomography.

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INTRODUCTION

Computed tomography (CT) is an unique technology to investigate microstructure. In this method, excessive sample preparation is not required before collecting 3D image data. Extreme dryness and exposure to high vacuum can therefore be avoided and the microstructure is preserved. The CT inspection of cementitious materials was pioneered using medical CT in 1980 [1]. In order to improve the image quality and obtain high resolution, CT scans were most often performed in high energy industrial facilities during the 1990s [2,3]. During the last 10 years, synchrotron radiation facilities have been utilized for related research, and a highest resolution of 0.44 mm was reached [4-7]. Recently, micro-CT has been applied to various characterizations of cementitious materials, including cement paste microstructure [4,5,7,8], durability [9-12], and fracture properties [13].

While the resolution obtained from synchrotron X-ray sources can reach below 1 mm, further studies on the details of sample microstructure for cementitious materials are still limited for several reasons. First, most synchrotron radiation facilities are established in national laboratories for testing of a wide range of materials, and accessibility to the equipment for a single type of material sampling is usually inadequate to perform quantitative analysis. Second, the specimens should be made extremely thin owing to attenuation of the X-ray signal, and this demands innovative techniques for the sample preparation.

In this study, an ultra-high resolution lab based nano X-ray CT was utilized. Using a high-flux laboratory X-ray source, this system can deliver the highest resolution of 50 nm. It provides an alternative yet accurate and convenient method to explore the cement microstructures. The equipment provides an alternative to synchrotron X-ray facilities for tomographic imaging.

EXPERIMENTS

Specimen preparation

A novel technique was developed for preparation of very thin samples. To investigate the interfacial transition zone (ITZ) between cement paste and “aggregate,” cement-gold foil specimens were made to stimulate the structure. ASTM Type I cement was sieved with an 75 micron filter to remove large cement grains. Cement paste with a water-cement ratio of 0.50 was mixed in a laboratory mixer for three minutes. A small amount of the paste was placed on gold foil which was placed on a microscope slide. A sandwiched sample was then formed as shown in Fig. 1 when another piece of microscope slide was placed on top of the material. Squeezing the sandwiched sample ensured a very thin layer of cement paste attaching to the gold foil. The glass slides specimens were clamped and cured in the moisture room until being tested at 1-day and 28-day. In the experiment, the region of interest was the interface between the gold surface and the cement paste. Gold foil was an attractive alternative because it offered a convenient way to achieve a very thin metallic layer. Signal attenuation is a major issue in these experiments, and thinness is very important. Before scanning, a very small slice of cement paste with gold foil was cut from the specimen.

Nanotomography measurement

The X-ray nanotomographic scans were performed at the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign. The X-ray source is a Cu rotating anode tube at fixed 8 KeV. A 64 mm (2.5 in.) field of view was chosen to compensate the tradeoffs between desire magnification and test sample scale, and the voxel resolution under this test setting was 64 nm.

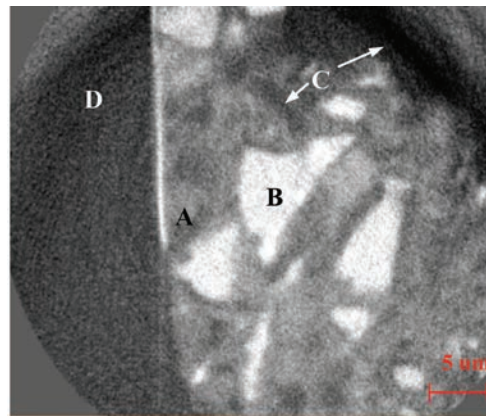


Fig. 1—Sampling schematic diagram.

RESULTS AND DISCUSSIONS

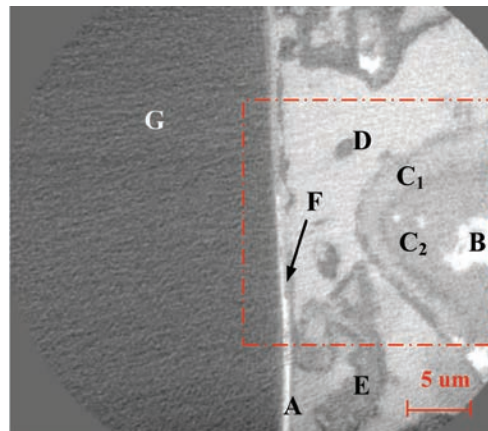
Overall appearance

Typical 2D images obtained from the samples in different ages (1-day and 28-day) are shown in Fig. 2 and Fig. 3. There are two main parts in the images. The microstructure of cement paste is visible on the right hand side, next to the narrow band of gold foil. The dark arc on the left is empty space. The red rectangle in Fig. 3 enclosed the area to construct the 3D images in Section 3.3.



A-Gold foil, B- Unhydrated Grain,
C-Porous area, D- Invalid area for CT

Fig. 2—Two-dimensional image at 1 day.



A-Gold foil, B- Unhydrated Grain,
C₁-Outer C-S-H, C₂-Inner C-S-H, D-Pore
E-Suspected Hadley grain, F-Micro crack,
G- Invalid area for CT

Fig. 3—2D image, 28-day.

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The cement microstructure part of images consist of several components in contrast. The brightest component is unhydrated cement grains. The darkest component is void space in the paste. The hydration products which include calcium hydroxide, C-S-H, Aft, and AFm phases are revealed in gray. These hydration products encircle the voids and unhydrated grains, and cannot be distinguished separately. The gold foil part is also shown as bright.

Details of the 2D images

Due to the high visibility of the gold foil in the image, it is easy to locate the ITZ on the right hand side. At early age (1-day), the “wall effect” [14] is observed with many bright unhydrated cement grains adjacent to the interface. The grain diameters are less than 20 mm (0.79 in.). Very small dark voids are revealed everywhere accompanying a big void of about 30-40 mm (1.18-1.57 in.) in the upper right corner of Fig. 2.

At later age (28-day), on the other hand, the images became brighter than before because the hydration of cement induced higher density paste (Fig. 3). It can be seen that there is less contrast between the different hydration products. Particle B in Fig. 3 is an unhydrated grain, one can also see regions of varying density of inner and outer C-S-H surrounding it. The coronal shell surrounds the particle in a manner that has been also described by Taylor [15] and Scrivener [16].

There are low density regions around original site of cement grains that are reminiscent of Hadley grains. On the bottom of Fig. 3 there is a suspected Hadley grain where the hydration products seem to be in layers of varying density.

A highly porous 0.2 mm (0.008 in.) wide gap is observed between the cement matrix and the gold foil. Diamond has found similar gaps in SEM images [17], which were considered to be possibly induced and enlarged by specimen preparation. Since the CT scan specimens in this study are perturbed very little by sample preparation before testing, it is reasonable to assign this gap to autogenous shrinkage cracking or incomplete debonding. Although this gap was as thin as 0.2 mm (0.008 in.), thin channels can still serve as percolated pathways through microstructure. These gaps at the interface increase the total pores content of ITZ.

Reconstruction of 3D images

As mentioned previously, an area in the 28-day age cement paste enclosed in the red rectangle shown in Fig. 3 was selected for 3D reconstruction. Software was used in this study for 3D reconstruction and quantitative image analysis. The resulting 3D images are shown in Fig. 4 and Fig. 5. Binary segmentation processes were applied to separate the different phases in cement paste. The bright end of the gray scale was interpreted as unhydrated grains. The darker part of the gray scale, on the other hand, was interpreted as pores. The middle part of the gray scale was assigned to other hydration products (including CH, C-S-H, Aft and AFm) that can only be seen jointly rather than be definitively segmented.

Figure 4 shows a 3D image of gold foil with only pores contained in the cement while Fig. 5 shows the entire cement paste with gold foil.

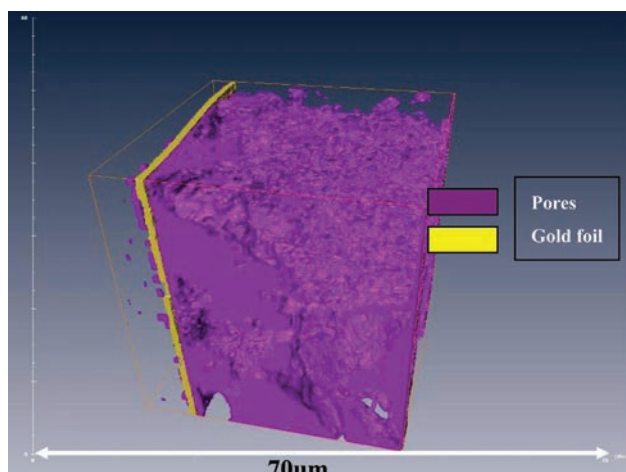


Fig. 4—Total pore network in a 28-day old cement paste.

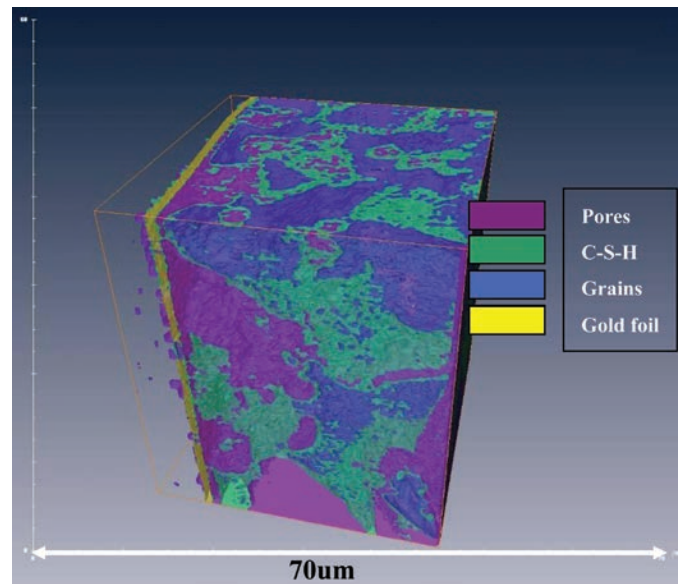


Fig. 5—Total cement microstructure in a 28-day old cement paste.

Quantitative Image Analysis of 3D images

A quantitative image analysis method was introduced by Scrivener [14] and Diamond [17]. Employing the method, consecutive 5 μm wide narrow strips were separated from the interface of foil-paste to the end of bulk paste, and the proportions of different components of paste microstructures were analyzed in the gray scale. Figure 6 illustrates the analysis concept. The analysis results are shown in Fig. 7 and 8.

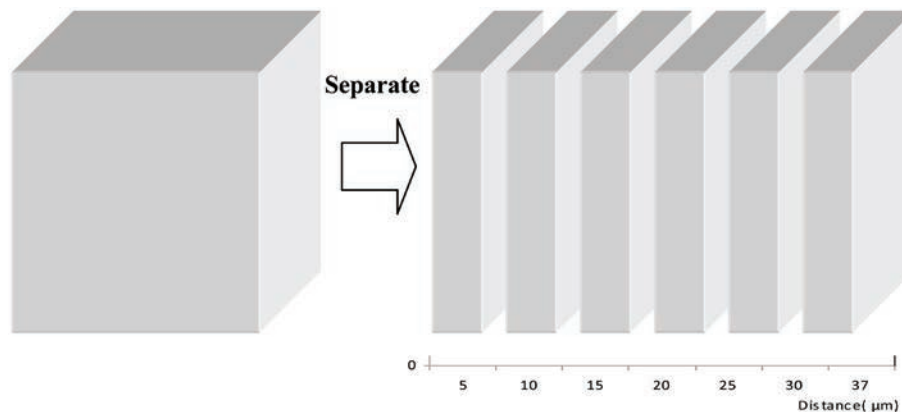


Fig. 6—Illustration of a paste separation.

The results provide evidence for a highly porous ITZ. In both the 1-day and 28-day scans, the distribution of porous shows some tendency to rise at the gold foil interface.

The results in Fig. 8 show that the percentage of the pores was initially more than 20% near the interface, and reduced further from the interface in the 28-day old paste. When the distance of the bulk from the gold foil was more than 30 mm (1.18 in.), the content of the pores was close to 5%. At the same time, the content of unhydrated grains and hydration products was increasing with respect to the distance further from the interface. The “wall effect” provides explanation for why particles are less present very near the interface. In the 28-day age, the hydration products fill the microstructure more completely.

One limitation of this study was the limited number of samples. Only one 1-day sample and one 28-day sample are discussed in this paper, although other work with more samples is ongoing. It should also

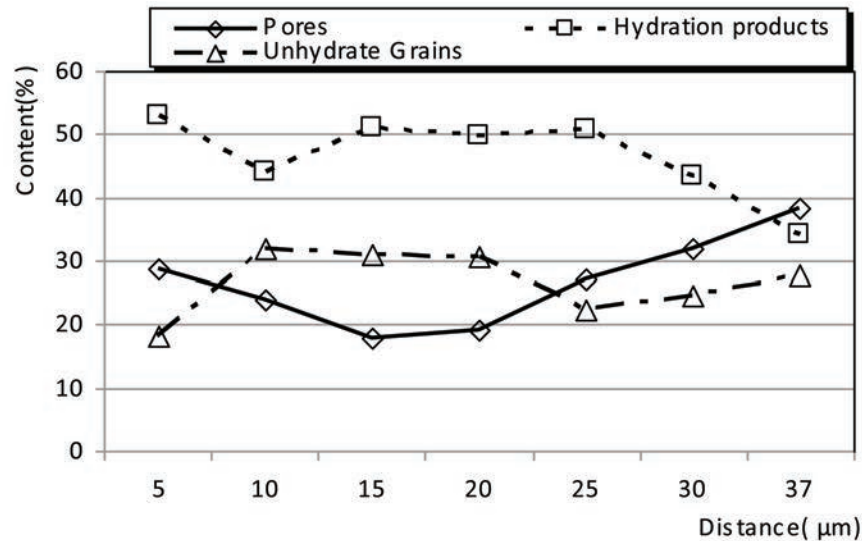


Fig. 7—Microstructure composition of 1-day old paste.

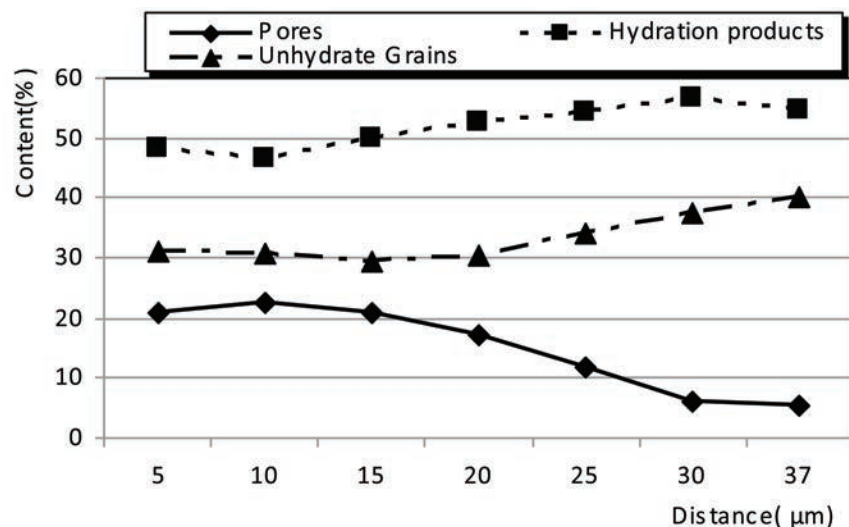


Fig. 8—Microstructure composition of 28-day old paste.

be noted that the gray-level thresholding method to separate and identify the different phases in the cement paste involves compromise, and therefore the values may be seen as approximations. Although the results of the content of different components seemed to be semi-quantitative, the trends in Fig. 8 provided useful insights.

CONCLUSIONS

X-ray nanotomography is an useful technique that provides 2D and 3D images of cement paste under conditions that minimize disturbance of microstructure development. In this study, images with very high spatial resolution of 64 nm were acquired. Encouraging results were achieved in this investigation of ITZ microstructure. The results provide insight into the size and composition of microstructure in the ITZ. The microstructure of the 28d sample reflected the impact of longer hydration time such as denser microstructure. Features such as Hadley grains could be observed. Variability of C-S-H density was observed.

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Closed-Form Solutions for Uniaxial Passive Restraint Experiments

by Z. C. Grasley

Synopsis: Uniaxially passive restraint experiments (for example, “cracking frames”) provide enough information to extract useful viscoelastic constitutive properties when combined with free deformation and mass loss experiments (in the case of drying shrinkage). In this paper, analytical techniques are described for deriving a closed-form solution to extract the viscoelastic Young’s modulus from solidifying concrete in a uniaxial passive restraint test. In addition, for the particular case where drying shrinkage is restrained in the test, approximate closed-form solutions are derived for the non-uniform internal relative humidity (RH), free drying shrinkage, and stress gradients. An example problem demonstrates the utility of the derived solutions.

Keywords: cracking frame; drying; restrained; solidification; viscoelastic.

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INTRODUCTION

Passive restraint tests have become increasingly popular as experimental methods for quantifying the sensitivity of certain concrete mixtures to cracking due to restrained free strains. Free strains, while typically drying (internal or external) shrinkage or thermal strains, can be any non load-induced strain. To date, passive restraint tests have been utilized primarily in a qualitative fashion such that information regarding the aging viscoelastic properties of the solidifying concrete is not directly determined from the tests. While the time to cracking in restrained concrete specimens is a beneficial parameter for screening concrete mixtures, passive restraint tests are also capable of yielding fundamental constitutive behavior of early-age, solidifying concrete.

Current passive restraint tests for concrete can be subdivided into two basic geometrical categories: uniaxial tests and ring tests. This paper will focus on uniaxial tests¹⁻⁶. The uniaxial test typically consists of a slender concrete beam with flared ends placed within a semi-rigid frame. The frame grips the flared ends and partially restrains the free movement of the concrete beam. Stress develops within the concrete, and, if the degree of restraint is high enough, the concrete will eventually crack and release the stress. Geometry of a typical passive restraint test is illustrated in Fig. 1. Often, the strain in the restraining bars of the frame is recorded as a function of time; this information may be used (along with the free strain and measured elastic Young's modulus history) to determine the aging viscoelastic Young's modulus of the concrete.

The objective of this paper is to derive closed-form analytical solutions for determining the solidifying, viscoelastic Young's modulus of concrete using data obtained from uniaxial passive restraint tests. Additionally, approximate analytical solutions for non-uniform stress gradients of symmetrically drying concrete will be derived as a function of the measured mass loss and spatially averaged free strain.

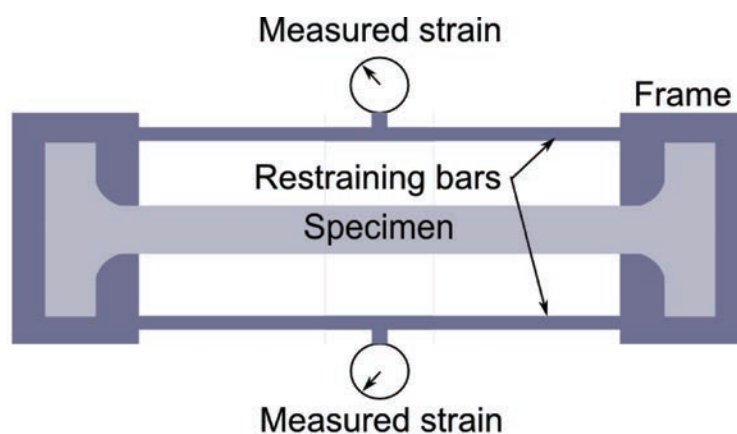


Fig. 1—Diagram of typical uniaxial passive restraint test.

RESEARCH SIGNIFICANCE

By extracting fundamental material properties from simple passive restraint tests, the utility of such tests increases substantially. Viscoelastic material properties obtained from passive restraint tests could be implemented in structural models to predict real stress distributions in concrete infrastructure, improving prediction of damage in such structures and providing a means for evaluating preventive measures such as extended wet curing, etc. In the remaining sections of this paper, a form of the solidifying viscoelastic constitutive equation allowing analytical solution of the uniaxial test will be introduced, and the solutions derived for both the viscoelastic Young's modulus and the non-uniform stress gradients.

CONSTITUTIVE MODEL

While Grasley and Lange⁷ have shown that the viscoelastic aging of cement pastes at early ages cannot be fully accounted for by the solidification theory, solidification is still the primary source of aging during this period. Thus, the constitutive equation for early age concrete can be approximated by the solidification theory⁸. According to the solidification theory, the constitutive equation of a solidifying viscoelastic material may be expressed according to

$$\dot{\varepsilon}(t) = \frac{E_0 \dot{\sigma}(t)}{v(t)} + \frac{1}{v(t)} \int_0^t J_g(t-t') \dot{\sigma}(t') dt' + \dot{\varepsilon}^f(t) \quad (1)$$

where t is elapsed time, $\varepsilon(t)$ is the time dependent uniaxial strain, E_0 is the elastic Young's modulus at an age where $v(t) = 1$, $\sigma(t)$ is the uniaxial stress, $v(t)$ is the aging function that represents the degree of solidification, $J_g(t)$ is the viscoelastic uniaxial compliance of the non-aging solid (that is solidifying), $\varepsilon^f(t)$ is the free strain, and the overhead dots denote the partial derivative with respect to time. The aging function $v(t)$ is unitless, has a value of zero at the time of set (or "time-zero"), and may be fit to the evolution of hydration data or the evolution of measured elastic moduli. For practical application, $v(t)$ is normalized to a value of 1 at whatever age E_0 and $J_g(t)$ are measured.

The presence of the time derivatives and integral preclude the direct implementation of Eq. (1) in elastic solutions for the passive restraint tests. A typical method of accounting for the time history dependence of viscoelastic materials in such a way as to allow use of existing elastic solutions is to utilize the elastic-viscoelastic correspondence principle⁹. The correspondence principle involves utilizing Laplace or Fourier transforms to eliminate differential operators, transforming the viscoelastic constitutive equation into the same form as for elastic materials. This transformation allows the direct use of elastic solutions for solving the transformed viscoelastic problem. Upon obtaining the solution in the transform domain, inversion yields the solution in the time domain. Unfortunately, the constitutive equation for solidifying materials does not allow use of the classic correspondence principle since it involves the product of a time-dependent function and a convolution integral, resulting in a convolution in the transform domain. In order to utilize the correspondence principle for solidifying materials, Grasley and Lange⁷ modified the classic correspondence principle, solving for the transformed strain as

$$\bar{\varepsilon}(s) = \sum_{i=1}^n \beta_i \frac{(s + \omega_i)^2}{s} \bar{J}_g(s) \bar{\sigma}(s + \omega_i) + \bar{\varepsilon}^f(s) \quad (2)$$

The overbars denote the Laplace transformed parameter with the transform parameter s , and the aging function expressed as

$$\frac{1}{v(t)} = \sum_{i=1}^n \beta_i e^{-\omega_i t} \quad (3)$$

where β_i and ω_i are fit parameters. Eq. (2) is in the same algebraic form as the elastic constitutive equation (i.e. a linear equation with no time derivatives or integrals), allowing one to utilize elastic solutions where the elastic strain is substituted by $\bar{\varepsilon}(s)$, the elastic uniaxial compliance replaced by $J_g(s)$, the stress replaced by $(s + \omega_i^2 \bar{\sigma})(s + \omega_i) \beta_i / s$, and the free strain replaced by $\bar{\varepsilon}^f(s)$.

Likewise, a modified correspondence principle (see Appendix A) may be used to solve the viscoelastic problem for a solidifying viscoelastic material with the constitutive equation written in terms of the strain history. If the aging function is expressed as

$$v(t) = \kappa (1 - \exp(-\lambda t)) \quad (4)$$

where κ and λ are fit parameters, one can write the transformed constitutive equation according to

$$\bar{\sigma}(s) = \kappa \bar{E}_g(s) \left\{ \left(s \bar{\varepsilon}(s) - (s + \lambda) \bar{\varepsilon}(s + \lambda) \right) - \left(s \bar{\varepsilon}^f(s) - (s + \lambda) \bar{\varepsilon}^f(s + \lambda) \right) \right\} \quad (5)$$

where $\bar{E}_g(s)$ is the Laplace transformed, non-aging viscoelastic Young's modulus of the solidifying material. As with Eq. (2), Eq. (5) is in the same algebraic form as its elastic equivalent. In the application of Eq. (5) with elastic solutions to solve for the transformed viscoelastic stress, the elastic Young's modulus is replaced by $\kappa \bar{E}(s)$, the elastic strain is replaced by $(s \bar{\varepsilon}(s) - (s + \lambda) \bar{\varepsilon}(s + \lambda))$, and the free strain is replaced by $(s \bar{\varepsilon}^f(s) - (s + \lambda) \bar{\varepsilon}^f(s + \lambda))$.

Since the solidification function has an equivalent effect on both viscoelastic and elastic moduli, the simplest way to obtain the aging function is to fit measured elastic moduli as a function of age, normalizing the function to unity at the age where E_0 is specified. If the age of initial displacement does not occur at $t = 0$, then Eq. (4) may be shifted such that $t = 0$ coincides with the initial displacement age. Shifting Eq. (4) may be accomplished according to

$$v(t) = \kappa (1 - \exp(-\lambda(t + t'))) \quad (6)$$

where t' is the age at initial displacement; with this modification, Eq. (5) becomes

$$\bar{\sigma}(s) = \kappa \bar{E}_g(s) \left\{ \left(s \bar{\varepsilon}(s) - (s + \lambda) \bar{\varepsilon}(s + \lambda) \right) / e^{\lambda t'} - \left(s \bar{\varepsilon}^f(s) - (s + \lambda) \bar{\varepsilon}^f(s + \lambda) \right) / e^{\lambda t'} \right\} \quad (7)$$

Inversion of Eq. (7) into the time domain yields $\sigma(t)$, where $t = 0$ corresponds to the time of initial application of displacement. Therefore, the actual age of a specimen at any time t is $t + t'$.

DEGREE OF RESTRAINT

The degree of restraint (of free deformation) is defined according to

$$\psi = \frac{u^f(t) - u(t)}{u^f(t)} \quad (8)$$

Therefore, the degree of restraint varies between 0 (free deformation) and 1 (fully restrained). Since the strain is considered to be axially uniform in the uniaxial test, the free displacement $u^f(t)$ and the total displacement $u(t)$ can be taken anywhere along the specimen length. For qualitative information such as "time to cracking", ψ must be higher than some minimum value necessary to induce cracking, but can approach 1. However, a proper ψ is critical for extracting quantitative, viscoelastic material properties from passive restraint tests. As $\psi \rightarrow 1$, the total strain measured in the restraint approaches 0; the accuracy of the measured strain is reduced as the value approaches the measurement precision. Therefore, ψ must be low enough to yield large enough deformation of the restraint to allow accurate determination of the strain magnitude. On the other hand, if ψ is too low, then the imposed stress level in the concrete is so low that there is very little mechanical deformation. A small magnitude of mechanical deformation results in poor accuracy in the extraction of mechanical properties.

DETERMINATION OF VISCOELASTIC YOUNG'S MODULUS

For the uniaxial passive restraint test, the non-aging elastic solution can be expressed as

$$\varepsilon(x, t) = \frac{\sigma(x, t)}{E_c} + \varepsilon^f(x, t) \quad (9)$$

where x is the spatial coordinate through the width of the specimen, $\varepsilon(x, t)$ is the total strain distribution, E_c is the Young's modulus of the concrete, $\varepsilon^f(x, t)$ is the free strain distribution, and $\sigma(x, t)$ is the axial stress. If we assume the total strain is constant across the specimen cross-section and that E_c is linear, then

$$\varepsilon(x, t) = \varepsilon(t) = \frac{1}{E_c} \int_0^L \sigma(x, t) dx + \int_0^L \varepsilon^f(x, t) dx = \frac{1}{E_c} \langle \sigma(t) \rangle + \langle \varepsilon^f(t) \rangle \quad (10)$$

where the $\langle \rangle$ indicate a spatially averaged value. For equilibrium and compatibility requirements, the force in the concrete must be equal to the force in the restraint system, and the strain in the restraint must match the strain in the concrete (since there is uniform strain assumed in both restraint and specimen) such that

$$\langle \sigma(t) \rangle = \frac{1}{L} \int_0^L \sigma(x, t) dx = \varepsilon(t) k \quad (11)$$

where $k = E_r \times A_c / A_r$ is the effective restraint stiffness, E_r is the Young's modulus and A_r the cross-sectional area of the axial restraint, and A_c the cross-sectional area of the concrete specimen. Often, uniaxial restraint tests are accompanied by free deformation specimens with the same cross-sectional dimensions and exposed to the same environmental conditions such that the average uniaxial free strain in the free and restrained specimens can be considered equivalent. The free strains could involve drying shrinkage, autogenous shrinkage, thermal dilatation, or a combination of several types. The average free strain is directly measured in the free specimen. Therefore, it is useful to combine Eq. (10) and (11), solving for E_c as

$$E_c = \frac{A_c \varepsilon(t) E_r}{A_r (\varepsilon(t) - \langle \varepsilon^f(t) \rangle)} \quad (12)$$

Note that for a non-aging elastic specimen, the time functions for the free and total strain will be equivalent, resulting in their cancellation and the maintenance of a constant E_c .

Rather than measuring the strain in the restraint, a load cell is often used with the restraint to determine stress directly¹⁰⁻¹¹. In this case,

$$E_c = \frac{\langle \sigma(t) \rangle}{\varepsilon(t) - \langle \varepsilon^f(t) \rangle} \quad (13)$$

Using Eq. (7) and (13), the non-aging viscoelastic modulus of the solidifying component of the concrete can be expressed in the transform domain according to

$$\bar{E}_g(s) = \frac{\langle \sigma(t) \rangle}{\kappa \left[\left(s \bar{\varepsilon}(s) - (s + \lambda) \bar{\varepsilon}(s + \lambda) / e^{\lambda t'} \right) - \left(s \bar{\varepsilon}^f(s) - (s + \lambda) \bar{\varepsilon}^f(s + \lambda) / e^{\lambda t'} \right) \right]} \quad (14)$$

Inversion of Eq. (14) into the time domain yields $E_g(t)$, which is the intrinsic, non-aging viscoelastic Young's modulus of the hydrating concrete. The bulk, aging viscoelastic Young's modulus of the solidifying concrete may be expressed according to¹²

$$E(t, t') = v(t') E_g(t - t') \quad (15)$$

where $v(t')$ is expressed according to Eq. (4).

While the preceding analysis assumes linearity of the time-dependent stress-strain response, it is known that the tensile response of concrete is nonlinear at high stress levels¹³. Additionally, no effort is made in the analysis to separate basic and drying creep components. Typical drying shrinkage tests involve high tensile stress near the surface due to the severe non-uniform shrinkage gradient. Even in the absence of external restraint, the internal restraint due to the gradient is enough to induce surface

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cracking when the surface is exposed to a sudden drop in RH¹⁴. It is likely that much of the nonlinearity (and much of the drying creep component) in the tensile viscoelastic response obtained from drying specimens is due to drying surface damage. Comparison of a viscoelastic Young's modulus of concrete obtained under test conditions suppressing surface damage to that obtained from the passive restrained drying shrinkage test could yield insight into the reduction in stiffness associated with the growth of damage. The integration of continuum damage mechanics with the analysis above would allow the determination of damage thresholds for ultimate failure for specific concrete mixtures.

NON-UNIFORM RH PROFILE

In order to determine $\varepsilon'(x,t)$ and $\sigma(x,t)$, $RH(x,t)$ must first be determined. For one dimensional Fickian drying of a long, prismatic specimen assuming a uniform initial RH ($RH_{initial}$), a constant boundary RH (RH_{bound}), and $RH(x,\infty) = RH_{bound}$,

$$RH(x,t) = RH_{bound} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{RH_{bound} \cos(n\pi) - RH_{bound}}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{Dn^2 \pi^2 t}{L^2}\right) + \frac{2RH_{initial}}{\pi} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{Dn^2 \pi^2 t}{L^2}\right) \frac{1 - \cos(n\pi)}{n} \quad (16)$$

where L is the shrinkage specimen width and D is the linear drying diffusion coefficient¹⁵. While it is widely recognized that concrete drying is nonlinear, a linear coefficient is considered here to make the solution tractable.

A simple expression for D may be obtained using measured mass loss due to drying. The derivation is included in Appendix B, with the final result as

$$D = \frac{L^2 \pi (RH_{initial}^2 - A + B)}{16(RH_{bound} - RH_{initial})^2 t} \quad (17)$$

where

$$A = \frac{215.726 RH_{initial} (\Delta m(t) + 0.75 \phi V \rho - 1)^{1/3}}{\phi^{1/3} V^{1/3} \rho^{1/3}} \quad (18)$$

and

$$B = \frac{11634.4 (\Delta m(t) + 0.75 \phi V \rho - 1)^{2/3}}{\phi^{2/3} V^{2/3} \rho^{2/3}} \quad (19)$$

In this case L is the thickness of the symmetrically drying mass-loss specimen, and $\Delta m(t)$ is the mass loss of the specimen at time t . V is the mass-loss specimen volume, ϕ is the pore volume fraction (porosity), and ρ is the density of water. The combination of Eq. (16) and (17) allows a simple approximation of internal RH distribution in drying concrete based on measured mass loss. It should be noted that Eq. (17) is an approximate model for the drying diffusion coefficient – not only is it limited by the assumptions already stated, but D is only valid in the early stages of drying, and assumes the desorption isotherm is represented by¹⁶

$$S(t) = 1 - 0.75 \left(1 - \left(\frac{RH}{98} \right)^3 \right) \quad (20)$$

It is well known that desorption isotherms of concrete vary significantly based on factors such as degree of hydration, w/c , and temperature. Therefore, is not universally applicable. However, a desorption

function in the form of or an alternate form could easily be fit to measured desorption data and the procedure outlined in Appendix B duplicated to determine an alternate expression for D .

Figure 2 shows the predicted average internal RH of a drying specimen using Eq. (17) compared to the exact analytical solution expressed by spatially averaging Eq. (16). Eq. (17) provides an accurate approximation until the average RH has dropped to about 1/2 the difference between $RH_{initial}$ and RH_{bound} .

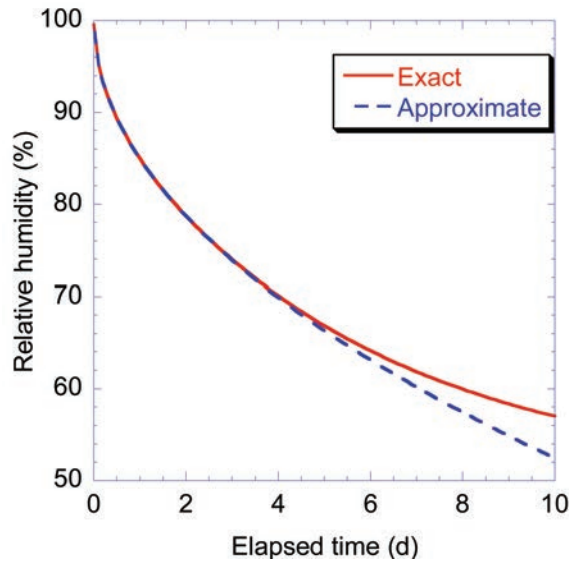


Fig. 2—Comparison of predicted average internal RH using exact solution for 1-day symmetric drying diffusion and early approximate solution (Eq. (17)). Prediction is for a specimen with $D = 1 \text{ cm}^2/\text{d}$ ($0.16 \text{ in.}^2/\text{d}$), $RH_{initial} = 100$, $RH_{bound} = 50$, and $L = 7.5 \text{ cm}$ (3 in.).

Non-uniform shrinkage and stress profiles

In order to extend the preceding analysis to determine the non-uniform stress distribution in concrete where the free strain is non-uniform, it is necessary to quantify $\varepsilon'(x, t)$. While this could be done numerically using finite element or finite difference techniques, it is the goal in this paper to derive a simple analytical technique to determine $\varepsilon'(x, t)$ as a function of the commonly measured $\langle \varepsilon'(t) \rangle$. The functions to be discussed are for drying shrinkage strain, but the same methodology could be utilized for thermal or other strains where the transport obeys Fickian behavior. For drying shrinkage, mass loss associated with symmetric drying of a prism or beam is needed to determine an approximate diffusion coefficient, while for thermal strains, the coefficient of thermal dilation is needed in order to determine $\varepsilon'(x, t)$. For the drying case, the procedure will be to determine an average drying diffusion coefficient based on the measured mass loss, then use this diffusion coefficient combined with the measured $\langle \varepsilon'(t) \rangle$ to predict $\varepsilon'(x, t)$.

Drying shrinkage of concrete occurs due to moisture transport from the inner core of concrete to an exposed surface with a boundary vapor pressure that is lower than that in the concrete. As moisture migrates from within the concrete to the surface, the internal relative humidity (RH) is reduced, resulting in negative capillary pressure in the pore fluid. The pore fluid pressure may be expressed according to the Kelvin-Laplace equation as

$$p_c = p_v - p = \frac{-\ln(RH / 100) RT}{v_m} \quad (21)$$

where p_c is the capillary pressure, p_v is the pressure in the gaseous phase, p is the pore fluid pressure, R is the universal gas constant, T is the temperature in kelvins, and v_m is the molar volume of water. Since changes in p_v are much smaller than for p , p_v is typically neglected. The result is that the local pore fluid pressure can be related directly to changes in the local internal RH. Note that RH is also affected

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by the presence of dissolved species in the pore fluid. However, for the sake of simplicity, the effect of dissolved species has been neglected in this derivation.

An additional source of drying shrinkage-inducing stress has been modeled by Coussy et al.¹⁷ The additional stress is associated with the development of new interfaces within the pore network of concrete as drying progresses, and is expressed as

$$U = \int_S^1 p_c(S') dS' \quad (22)$$

where S is the degree of fluid saturation of the pore network. According to Coussy et al., U acts as an effective pressure; therefore, the total pressure in the pore fluid may be expressed as

$$\xi(t) = S(t)p_c + U(t) \quad (23)$$

Elastic principle strain in saturated porous bodies subjected to an internal pore pressure can be determined using Biot's poroelastic theory¹⁸ according to

$$\varepsilon = \frac{p}{3} \left(\frac{1}{K} - \frac{1}{K_s} \right) \quad (24)$$

where K is the bulk modulus of the porous body, K_s is the bulk modulus of the solid phase of the material. For concrete drying shrinkage, the effective pore pressure ξ may replace p in Eq. (24) to obtain

$$\varepsilon(t) = \frac{\xi(t)}{3} \left(\frac{1}{K} - \frac{1}{K_s} \right) \quad (25)$$

An alternative poromechanical approach to modeling shrinkage of porous materials to that outlined above has recently been published by Vlahinic et al.¹⁹, and involves accounting for partial saturation by reducing K_s proportionally. The model framework derived in this paper could easily be applied to this alternative approach instead of the approach of Coussy et al.

While it is suggested that drying shrinkage is a viscoelastic response²⁰⁻²¹, if we assume linearity of the response, then the drying history effect is the same for both $\varepsilon^f(x,t)$ and $\langle \varepsilon(t) \rangle$. Therefore, we can simplify the derivation by cancelling the history effect, and simply use an elastic solution for $\varepsilon^f(x,t)$ by combining Eq. (23) with Eq. (25). $S(t)$ can be approximated by eq. (20) and $\varepsilon^f(x,t)$ may be written according to

$$\varepsilon^f(x,t) = \xi(x,t)M \quad (26)$$

where M is a function of the mechanical properties of the concrete. In order to determine the non-uniform drying shrinkage profile in a symmetrically drying specimen, the diffusion coefficient (as determined in Appendix B) and the parameter M (see Eq. (26)) must be known. Appendix C derives the parameter M as a function of the spatially averaged free shrinkage strain as

$$M = \frac{0.4L \langle \varepsilon^f(t) \rangle}{\sqrt{D} \sqrt{t} (RH_{initial} - RH_{bound})} \quad (27)$$

with units of 1/MPa (x 6.9 1/ksi). To determine the non-uniform drying shrinkage profile in the time domain, Eq. (27) may be combined with Eq. (16), (17), (23), and (26).

In order to determine the non-uniform stress profile in a drying specimen where solidification and viscoelasticity are considered, it is necessary to determine the free shrinkage strain profile in the transform domain. The transformed free strain may be determined by transforming Eq. (26) and (44) to obtain

$$\bar{\varepsilon}^f(x, s) = 1.1 \left(\frac{RH_{initial}}{s} - \overline{RH}(x, s) \right) M \quad (28)$$

where $\overline{RH}(x, s)$ is determined in Appendix C by Eq. (38). To determine the non-uniform stress profile in either the restrained or unrestrained (free) case, Eq. (7) may be used. In the unrestrained case, the measured strain is the average free strain (assuming a long, slender beam-like shrinkage specimen). Inversion of Eq. (7) into the time domain yields $\sigma(x, t)$.

EXAMPLE

As an example problem, consider a passive uniaxially restrained test of drying concrete where the passive restraint is applied at an age of $t' = 1$ d (drying also starts at 1 d). The specimen width in the drying direction is 7.5 cm (3 in.), and is subjected to a 50% RH and 20°C (68°F) environment. Assume the measured axial average stress history is

$$\langle \sigma(t) \rangle = 1 - \exp(-t/5) \text{ MPa (x 145 psi)} \quad (29)$$

and the average measured axial free strain history is

$$\langle \varepsilon^f(t) \rangle = -(1 - \exp(-t/9.5)) 500 \times 10^{-6} \quad (30)$$

If the degree of restraint is assumed to be $\psi = 0.5$ for the duration of the test, then the average measured axial strain is $\langle \varepsilon(t) \rangle = 0.5 \langle \varepsilon^f(t) \rangle$. Assume the aging parameters are $\kappa = 1.7$ and $\lambda = 0.3$. With the preceding information, the transformed non-aging viscoelastic Young's modulus of the solidifying gel can be determined by using Eq. (14). Inversion into the time domain yields

$$E_g(t) = 2.913 + 12.76e^{-1.26t} + 1.578e^{-0.2t} \text{ GPa (x 145 ksi)} \quad (31)$$

and the application of Eq. (15) with Eq. (4) and (31) yields $E(t, t')$.

In order to determine $\varepsilon^f(x, t)$ and $\sigma(x, t)$, the effective diffusion coefficient must be determined according to Eq. (17), and M according to Eq. (46). If the mass loss can be expressed as

$$\Delta m = 59.6(1 - e^{-t/4.313}) \times 10^{-3} \text{ kg (x 2.2 lb)} \quad (32)$$

$\phi = 0.18$, $V = 1.547 \times 10^{-3} \text{ m}^3$ (x 35.3 ft³), and $\rho = 1000 \text{ kg/m}^3$ (x 0.0625 lb/ft³), then the application of Eq. (17) results in an expression for $D(t)$. Next, the use of Eq. (46) results in an expression for $M(t)$. Combination of Eq. (16) and the expression for $D(t)$ results in $RH(x, t)$, the results of which are illustrated in Fig. 3. After the determination of $D(t)$, $M(t)$, and $RH(x, t)$, $\varepsilon^f(x, t)$ may be determined according to the process outlined in the previous section. For this example problem, the predicted $\varepsilon^f(x, t)$ are plotted in Fig. 4. The progressively higher shrinkage on the surface at later ages (despite the constant RH_{bound}) is attributable to viscoelastic effects.

The stress profile for the example problem must be determined first in the transform domain. The transformed shrinkage profile may be determined by Eq. (28), then input into Eq. (7) to obtain $\bar{\sigma}(x, s)$; inversion into the time domain results in the restrained drying stress profiles for solidifying, viscoelastic concrete shown in Fig. 5. As expected, the stress profiles indicate compression in the center of the symmetrically drying specimen, and tension in the near-surface zones. It is interesting to note, however, that the stress at the surface is actually less than the zone slightly beneath the surface. This effect is likely attributable to the combined effects of viscoelasticity and solidification. Since the surface displacement (from shrinkage) is applied at a very early age, there is substantial opportunity for the surface stress to be relaxed by viscoelastic effects. Additionally, the model predicts significant solidification occurs at the surface after the initial surface displacement. The hydration products that form after the displacement is first applied (from shrinkage) form in a stress-free state, and thus may even

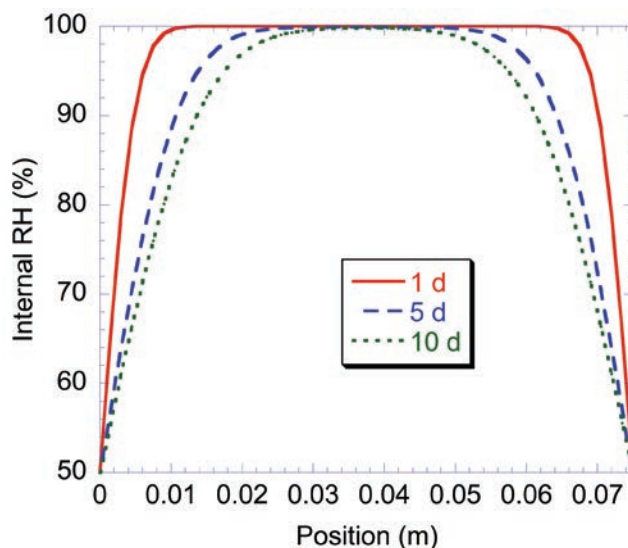


Fig. 3—Modeled internal RH profile at 1 day, 5 days, and 10 days after initiation of drying. (Note: 1 m = 3.281 ft.)

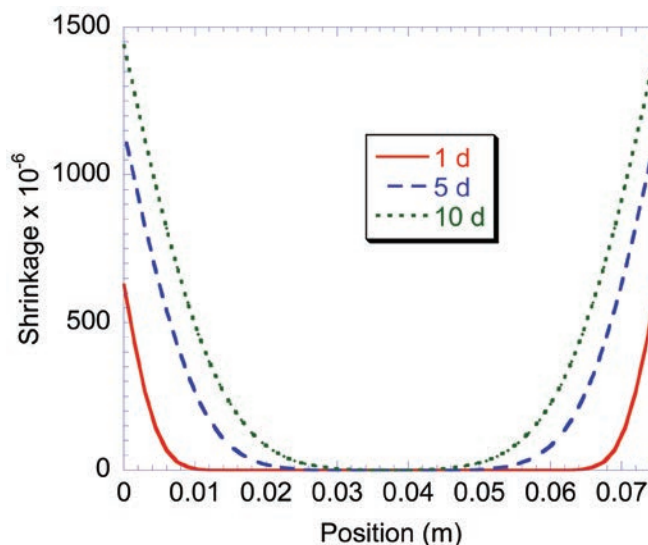


Fig. 4—Modeled drying shrinkage profiles at 1 day, 5 days, and 10 days after initiation of drying. (Note: 1 m = 3.281 ft.)

go into compression as drying progresses. In reality, the amount of surface hydration (and thus solidification) after the onset of drying will be limited since hydration slows considerably at RH below 80%²². Therefore, surface curvature of the stress profiles in Fig. 5 is likely exaggerated.

SUMMARY

Closed-form analytical solutions have been derived that allow the extraction of the viscoelastic Young's modulus of solidifying concrete from a typical uniaxial passive restraint experiment. In addition, approximate solutions have been presented for predicting the internal RH, drying shrinkage, and stress profiles for a symmetrically drying prismatic/beam specimen. The example presented in the previous section shows calculated profiles for typical test conditions and a representative material. Viscoelastic effects result in a model predicted time-dependent increase in surface shrinkage strain even with a constant boundary RH. Likewise, combined viscoelastic and solidification effects result in a model predicted shift of maximum tensile stress inward from the drying surface as drying progresses.

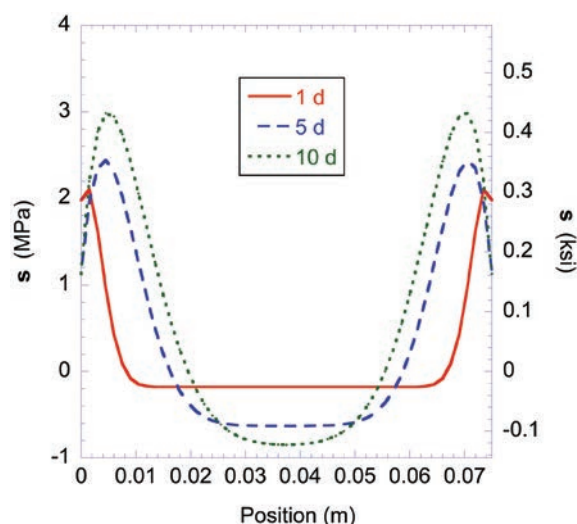


Fig. 5—Modeled stress profiles in restrained shrinkage specimen ($\psi = 0.5$) at 1 day, 5 days, and 10 days after initiation of drying. (Note: 1 m = 3.281 ft.)

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NOTATIONS, DEFINITIONS, AND SYMBOLS

A_c	= cross-sectional area of restrained concrete
A_r	= cross-sectional area of restraint
D	= diffusion coefficient
RH	= relative humidity
E	= viscoelastic Young's modulus of concrete
E_0	= Young's modulus at age where $v(t) = 1$
E_c	= Young's modulus of concrete
E_c^g	= non-aging viscoelastic Young's modulus of the solid phase of solidifying concrete
E_r^g	= Young's modulus of restraint
$\bar{f}$	= Laplace transform of $f(t)$
J^g	= uniaxial viscoelastic compliance
K	= bulk modulus of concrete
K_s	= bulk modulus of the solid phase of concrete
k	= effective restraint stiffness
L	= width of specimen in the direction of symmetric drying
p	= pore fluid pressure
p_c	= capillary pressure
p_v	= vapor pressure
R	= universal gas constant
RH_{bound}	= constant boundary RH
$RH_{initial}$	= initial internal RH prior to drying
S	= saturation
s	= transform variable
T	= temperature
t	= time
t'	= age of initially applied displacement
U	= pore pressure associated with interfaces
V	= volume of mass-loss specimen
x	= spatial coordinate
Δm	= mass loss
ε	= strain
ε^f	= free strain
ϕ	= porosity
ρ	= density of water
σ	= stress
$v(t)$	= aging function
v_m	= molar volume of water
$\omega, \beta, \kappa, \lambda$	= fit parameters for aging function
ξ	= effective pore pressure
ψ	= degree of restraint

APPENDIX A

The constitutive equation for the stress history of a solidifying, linear viscoelastic material may be expressed by¹²

$$\sigma(t) = \int_0^t v(t') \frac{\partial \varepsilon(t')}{\partial t'} E_g(t-t') dt' \quad (33)$$

If the aging function is expressed according to Eq. (4), then the constitutive equation becomes

$$\sigma(t) = \kappa \int_0^t (1 - e^{-\lambda t'}) \frac{\partial (\varepsilon(t') - \varepsilon^f(t'))}{\partial t'} E_g(t-t') dt' \quad (34)$$

Taking the Laplace transform of Eq. (34) and utilizing the complex shift theorem, the transformed stress is obtained as

$$\bar{\sigma}(s) = \kappa \bar{E}_g(s) \left[s \left(\bar{\varepsilon}(s) - \bar{\varepsilon}^f(s) \right) \right] - \kappa \bar{E}_g(s) \left[(s + \lambda) \left(\bar{\varepsilon}(s + \lambda) - \bar{\varepsilon}^f(s + \lambda) \right) \right] \quad (35)$$

which simplifies to Eq. (5).

APPENDIX B

The diffusion coefficient of a symmetrically (from two parallel sides) drying prism or beam with a uniform initial RH ($RH_{initial}$) exposed to a constant ambient RH (RH_{bound}) may be approximated by the measured mass loss. If we approximate the drying process with a linear diffusion coefficient, then the governing equation, boundary conditions, and initial condition are:

$$\begin{aligned} \frac{\partial RH(x,t)}{\partial t} &= D \left(\frac{\partial^2 RH(x,t)}{\partial^2 x} \right) \\ RH(0,t) &= RH_{bound} \\ RH(L,t) &= RH_{bound} \\ RH(x,0) &= RH_{initial} \end{aligned} \quad (36)$$

Equation (36) may be readily solved in the Laplace Transform domain. Transforming Eq. (36) results in

$$\begin{aligned} s \bar{RH}(x,s) - RH_{initial} &= D \left(\frac{\partial^2 \bar{RH}(x,s)}{\partial^2 x} \right) \\ RH(0,t) &= RH_{bound} / s \\ RH(L,t) &= RH_{bound} / s \end{aligned} \quad (37)$$

The solution to Eq. (37) is

$$\bar{RH}(x,s) = \frac{e^{\frac{\sqrt{s}x}{\sqrt{D}}}}{\left(1 + e^{\frac{L\sqrt{s}}{\sqrt{D}}}\right)s} \left[\left(e^{\frac{L\sqrt{s}}{\sqrt{D}}} + e^{\frac{2\sqrt{s}x}{\sqrt{D}}} \right) (RH_{bound} - RH_{initial}) + \left(e^{\frac{\sqrt{s}x}{\sqrt{D}}} + e^{\frac{\sqrt{s}(L+x)}{\sqrt{D}}} \right) RH_{initial} \right] \quad (38)$$

The spatially averaged RH is related directly to the mass loss of the specimen. Therefore we solve for $\langle \bar{RH}(s) \rangle$ as

$$\langle \bar{RH}(s) \rangle = \frac{RH_{initial}}{s} + \frac{2\sqrt{D} (RH_{bound} - RH_{initial}) \tanh\left(\frac{L\sqrt{s}}{2\sqrt{D}i}\right)}{Ls^{3/2}} \quad (39)$$

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Equation (39) is not particularly useful in its present form as it is not analytically invertible back into the time domain. However, if we focus on early drying behavior, we find that we can simplify Eq. (39) using the initial value theorem of Laplace transforms; this theorem states that

$$f(0^+) = \lim_{t \rightarrow 0^+} f(t) = \lim_{s \rightarrow \infty} s \bar{f}(s) \quad (40)$$

As $s \rightarrow \infty$, the $\tanh$ term in Eq. (39) rapidly approaches 1 such that for early drying we may write

$$\langle \overline{RH}(s) \rangle \approx \frac{RH_{initial}}{s} + \frac{2\sqrt{D} (RH_{bound} - RH_{initial})}{Ls^{3/2}} \quad (41)$$

which may be analytically inverted to obtain

$$\langle RH(t) \rangle = RH_{initial} - \frac{4\sqrt{D} (RH_{bound} - RH_{initial}) \sqrt{t}}{L\sqrt{\pi}} \quad (42)$$

The mass loss due to drying is almost entirely induced by loss of liquid water (mass loss of vapor is negligible). Therefore,

$$\Delta m = (1 - S) \phi V \rho \quad (43)$$

where S is a function of the average internal RH such that $S = S(\langle RH(t) \rangle)$. Combining Eq. (20), (42), and (43), one may solve for D to obtain the expression shown in Eq. (17) of the text.

APPENDIX C

In order to determine the non-uniform drying shrinkage profile in a symmetrically drying specimen, the diffusion coefficient (as determined in Appendix B) and the parameter M (see Eq. (26)) must be known. To approximate M , the measured spatially averaged drying shrinkage may be utilized. Using the desorption isotherm shown in Eq. (20), one can show that the effective pore pressure ξ (obtained from Eq. (23)) can be approximated by a linear function according to

$$\xi \approx 1.1 \times \delta RH \text{ MPa (x 145 psi)} \quad (44)$$

at room temperature, where $\delta RH = RH_{initial} - \langle RH(t) \rangle$. Figure 6 shows the quality of fit of the approximate function. As the drying shrinkage is expressed by Eq. (26), the parameter M may be solved for as

$$M = \frac{\langle \varepsilon^f(t) \rangle}{1.1 \delta RH} \quad (45)$$

and may be combined with Eq. (42) to obtain

$$M = \frac{0.4L \langle \varepsilon^f(t) \rangle}{\sqrt{D} \sqrt{t} (RH_{initial} - RH_{bound})} \quad (46)$$

with units of 1/MPa (x 6.9 1/ksi).

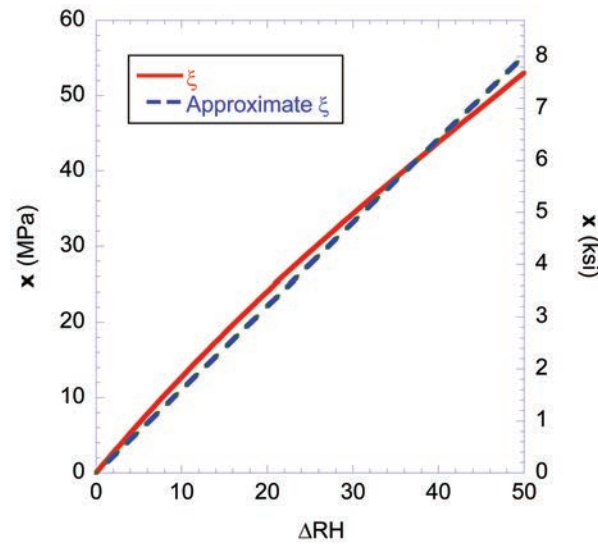


Fig. 6—Comparison of actual effective pore pressure (ξ) determined from Eq. (23) with approximate function shown in Eq. (23).

Applications of Electrical Impedance Methods in Linking Structure of Micro- and Macro-Porous Concretes to Their Transport Properties

by N. Neithalath and J. Jain

Synopsis: Electrical impedance based methods are frequently used to monitor the microstructural development in cement-based materials due to their non-invasive nature and the ability to make continuous measurements. This paper discusses two other applications of electrical impedance for two different classes of concretes—micro-porous conventional concretes and macro-porous pervious concretes. The effectiveness of a microstructural parameter derived from electrical impedance data to relate to the rapid chloride transport parameters of conventional concretes is described. The influence of the non-steady state migration test in changing the microstructure of concretes due to formation of new solid products through chloride binding of cement hydrates is also evaluated in detail through a combination of measured electrical impedance parameters and an equivalent electrical circuit model. The values of the components of the model determined before and after the migration test provide confirmation of the formation of binding products along the pore walls in concrete. Electrical impedance observations along with a modified Bergman equation are used to predict the porosity of pervious concretes. The experimentally determined and predicted porosities match adequately. The effective electrical conductivity can also be used in well known permeability prediction equations such as the Kozeny-Carman or Katz-Thompson equations for performance prediction of pervious concretes.

Keywords: chloride transport; electrical impedance spectroscopy; permeability; pervious concrete; pore connectivity; pore structure; porosity.

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INTRODUCTION

Understanding the influence of material parameters, and placing and curing conditions on the microstructure development of cement-based materials is essential towards reliably predicting the material performance. Among several methods that allow continuous monitoring of the microstructure of cement-based materials, electrical impedance based methods have received significant attention in the past¹⁻³. The cement paste is electrically conductive by virtue of its interconnected pore network filled with the pore solution containing ions released from the cement. During hydration, the volume and connectivity of the pore network, as well as the conductivity of the ionic pore solution changes with time. Such a behavior allows the use of dielectric response of the material (electrical conductivity or dielectric permittivity) as a tool to monitor microstructural changes with time. Recent studies⁴ have used electrical impedance data along with established models such as Archie's law or percolation theory to predict the porosity and thus the compressive strengths of cement pastes and concretes. A few studies have also reported the use of EIS in the determination of chloride diffusivity in concretes⁵, characterization of conductive fiber reinforced composites⁶, and monitoring damage in cement composites during loading⁷, thus making this method one of the most versatile non-invasive property determination techniques for cement-based materials.

In electrical impedance spectroscopy (EIS), the measured current response of the sample to the applied voltage (typically in the mV range) contains both the phase and amplitude components. The frequency dependent measured impedance of the system $Z(\omega)$ is a complex quantity with the real part, $Z'(\omega)$ (equal to $|Z| \cos \theta$), representing the in-phase component, and the imaginary part, $Z''(\omega)$ (equal to $|Z| \sin \theta$), representing the out-of-phase component. The plot of real versus imaginary impedance for the entire range of frequencies is called the Nyquist plot, a typical example of which is shown in Fig. 1. The response of the system, at a minimum, consists of the response of the bulk material and the electrodes. The meeting point of the bulk and electrode arcs in this plot is termed the bulk resistance of the sample from which the conductivity (at the frequency corresponding to the bulk resistance) of the bulk specimen can be obtained. $Z(\omega)$ can be used to determine the frequency dependent dielectric permittivity, $\varepsilon(\omega)$, and electrical conductivity $\sigma(\omega)$ as

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \frac{1}{j\omega \varepsilon_0 Z(\omega)(A/d)} \quad (1)$$

$$\sigma(\omega) = \varepsilon''(\omega)\omega \varepsilon'(\omega) \quad (2)$$

$\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary components of dielectric permittivity, ε_0 is the dielectric permittivity of free space (8.845×10^{-12} F/m), and A/d is the measurement cell geometry factor.

The major objective of this paper is to demonstrate the use of electrical impedance spectroscopy along with: (i) equivalent electrical circuit models for material microstructure, or (ii) analytical models for material structure that uses dielectric response features, to provide indicators of the relationship between material structure and relevant transport properties of conventional concretes (micro-porous) or pervious concretes (macro-porous). For conventional concretes, the relationships between common rapid chloride transport parameters (rapid chloride permeability as per ASTM C1202, and non-steady

state migration as per NT Build 492⁸) and a microstructural parameter derived from effective electrical conductivity are examined. Limited data exists on the influence of applied electrical field in chloride binding⁹. While chloride binding in steady-state migration conditions has been quantified, no data exists with respect to non-steady state conditions¹⁰. Therefore an equivalent electrical circuit model for concrete microstructure is also used in conjunction with the impedance data to evaluate the changes in microstructure due to chloride binding in rapid non-steady state migration testing.

For pervious concretes, which are primarily designed to facilitate run-off reduction and reduce tire-pavement interaction noise, the porosity and pore network connectivity are the important pore structure parameters that impact their transport behavior. An analytical form of Bergman's equation for two-phase composite media that uses the dielectric properties is used in this paper for porosity prediction of pervious concretes. Among several effective media theories for dielectric dispersion, Bergman's equation was chosen because of the implicit hypothesis of small grain contact area—that is, the assumption that the contact area with the neighboring grains is small compared to the grain size—that fits well with the material structure of pervious concretes. The use of effective conductivity obtained from impedance towards the prediction of permeability in such systems is also detailed.

EXPERIMENTAL PROGRAM

Materials and mixture proportions

Type I ordinary portland cement conforming to ASTM C150 was used to prepare all the concrete mixtures in this study. The supplementary cementing materials used for certain mixtures are either a Class F fly ash conforming to ASTM C618 or a commercial dry densified silica fume (SF) conforming to ASTM C1240. The replacement of cement by fly ash was carried out at dosages of 10% and 20% by mass (referred to as FA 10 and FA 20 in the graphs), and for silica fume, the cement replacement levels were 6% and 9% by mass (referred to as SF 6 and SF 9 in the graphs). The physical and chemical characteristics of the cement replacement materials can be found in Table 1. All the concrete mixtures were prepared using a water-cementitious material ratio (w/cm) of 0.40. Commonly adopted mixing procedures were employed for all these mixtures, which were cured until 90 days in a moist environment with a greater than 98% relative humidity. Six cylinders (4 x 8 in. [100 x 200 mm]) were made for each mixture for the rapid chloride transport tests at several ages.

The pervious concrete mixtures that are used in this study were extracted from a larger experimental set, designed to evaluate the hydraulic, acoustic, and mechanical properties of this novel construction material^{11,12}. The mixtures were made using single-sized aggregates and their binary blends. The single-sized aggregates had nominal maximum sizes of 4.75, 9.5, or 12.5 mm (0.19, 0.38, or 0.50 in.). The binary blends were prepared by replacing 25, 50, and 75% by weight of the larger aggregates with the smaller aggregates. The water-cement ratio was maintained at 0.33 for all these mixtures, and the cement content was adjusted so as to ensure that no residual paste clogs the pore space. The resultant aggregate-cement ratio ranged from 5.5 to 5.7 for all the pervious concrete mixtures.

Experimental determination of porosity

The porosities of concretes were determined at desired ages using a vacuum saturation method outlined in a RILEM standard¹³. The porosities of pervious concretes were determined using a volumetric method and an image analysis procedure. In the volumetric method, the cylindrical pervious concrete specimens (100 mm [4 in.] in diameter and 150 mm [6 in.] long) were immersed in water for 24 hours to saturate the pores in the matrix. After removal from water, the sample was enclosed in a latex membrane and the bottom of the specimen was sealed to a stainless steel plate. The mass of this system was measured. Water was added to the top of the sample until it was filled, which indicated that all the interconnected pores were saturated. The volume of water needed to fill the specimen, expressed as a percentage of the total volume of the specimen, is reported as the total porosity. Three pervious concrete specimens belonging to the same mixture were tested for porosity and the average values reported. In the image analysis method, two pervious concrete specimens belonging to the same mixture were sectioned at different depths. The surface of each section was scanned using a flat bed scanner, and an image conditioning and feature measurement procedure using a commercial software was employed to estimate the fractional area of pores. The average of fractional pore areas of all sections is taken as the specimen porosity. According to stereological theory, if random samples are used, the volumetric

porosity should be similar to the area fraction of pores from two-dimensional image. This has been rigorously verified in a previous work by the first author and colleagues¹⁴. Similar image analysis methods can be used to extract other pore structure features of pervious concretes such as the characteristics pore sizes, specific surface areas, and mean free spacing of pores^{14,15}.

Determination of chloride transport parameters

The chloride transport behavior of concretes is ascertained in this study through the use of rapid test methods such as the rapid chloride permeability (RCP) test in accordance with ASTM C1202 and non-steady state migration (NSSM) test in accordance with NT Build 492. Concrete specimens cured for 28, 56, or 90 days in saturated conditions were used for the transport tests. The charge passed through the concrete under the RCP test provides an indication of the resistivity or conductivity of the concrete, which is in turn expressed as an index of the penetrability of chloride ions into concrete. The catholyte and anolyte solutions used were 3% NaCl and 0.3 N NaOH for the RCP test, and 10% NaCl and 0.3N NaOH for the NSSM test. RCP test was carried out for a duration of 6 hours under a 60 V DC potential whereas the duration and applied potentials for the NSSM test depends on the initial value of current that passes through the specimen. NT Build 492 provides these parameters. The chloride penetration depth in the specimens subjected to NSSM test was determined using a colorimetric method, from which the non-steady state migration coefficients can be determined. Detailed procedure and application for several concrete mixtures can be found in other publications^{8,16,17}.

Electrical impedance spectroscopy (EIS)

Electrical Impedance Spectroscopy (EIS) measurements were performed using a gain-phase analyzer. Alligator plugs from the impedance analyzer were attached to the electrodes. The impedance measurements were carried out over a frequency range of 0.1 Hz to 1 MHz using a 250 mV AC signal with 10 measurements per decade. A typical Nyquist plot is shown in Fig. 1. From the bulk resistance (R_b) of the sample (the real coordinate of the meeting point of bulk and electrode arcs in a Nyquist plot), the effective conductivity (σ_{eff}) is calculated as

$$\sigma_{eff} = \frac{l}{R_b A} \quad (3)$$

In the above expression, l is the spacing between the electrodes, and A is the cross sectional area.

For the concrete specimens, the EIS measurements were performed on specimens used for RCP and NSSM tests before and after the transport tests were performed. The specimen cells containing the specimen and the corresponding electrolytes were used for EIS measurements. The effective specimen conductivity was calculated using Eq. (3).

For the electrical impedance measurements of pervious concretes, the specimen was enclosed in a latex membrane and the bottom sealed to a stainless steel plate electrode using silicone sealant, with a piece of porous foam in between the specimen and the plate electrode to ensure proper electrical contact. After the specimen was saturated with the electrolyte, another stainless steel plate with a small acrylic dyke was placed at the top of the specimen, with a piece of porous foam in between. A schematic of the test set up, along with detailed explanations can be found in earlier publications^{12,15}. The porous specimen was filled with the electrolyte (3% NaCl), and the impedance measurements were carried out. The effective conductivity (σ_{eff}) was calculated using Eq. (3) in this case also.

ELECTRICAL IMPEDANCE DATA AND MODELS APPLIED TO CONVENTIONAL CONCRETES

It has been well established that electrical impedance spectroscopy (EIS) can be used to monitor the hydration process of cementitious materials^{1,2,18}. Recent studies have also examined the use of effective electrical conductivity obtained from Nyquist plots of the impedance data, and its time derivative to determine the setting times of cement pastes¹⁹. A few studies^{5,20} have also investigated the chloride diffusivity in concretes through EIS. The focus of this section of the paper, therefore, is on the use of electrical impedance measurements along with models to quantitatively determine the features of the concrete microstructure such as the porosity and pore connectivity, or the changes that occur in the

concrete system as a result of chloride ingress under forced electro-migration tests, which are typically used to study chloride transport.

Linking rapid chloride transport parameters to the material microstructure through impedance measurements

The effective conductivity (σ_{eff}) of a fluid filled porous medium such as concrete can be expressed as a function of the conductivity of the fluid phase in the pores (σ_{pore}), the specimen porosity (ϕ), and the pore connectivity factor (β) as

$$\sigma_{\text{eff}} = \sigma_{\text{pore}} \phi \beta \quad (4)$$

The effective conductivity can be determined from the Nyquist plots using Eq. (3). The pore solution conductivity (σ_{pore}) is not very easy to experimentally determine, though methods of pore solution extraction and conductivity measurements have been carried out²¹. The pore solution conductivities of the different concrete mixtures were determined from the equivalent ionic conductivities of the highly conductive species in the pore solution (OH^- , Na^+ , K^+), the ionic concentrations, and the species valences, which has been provided in an easy-to-use using a web interface (<http://ciks.cbt.nist.gov/poresolnalc.html>). The ionic concentration was obtained from the cement and the replacement materials content, w/cm , and the degrees of hydration. The overall degrees of hydration of the pastes containing supplementary cementing materials at desired ages were obtained from the non-evaporable water contents of cement pastes made using the same w/cm as the concretes, using the model²² given below

$$\alpha_T = \left[\frac{(w_n)_{c-0}}{(w_n)_{c-\infty}} \right] m_c + \left[\frac{(w_n)_{c-r}}{(w_n)_{c-\infty}} \right] m_c + \left[\frac{(w_n)_r}{(w_n)_{r-\infty}} \right] m_r \quad (5)$$

In the above equation, α_T is the total degree of hydration in pastes containing cement replacement materials, $(w_n)_{c-0}$, $(w_n)_r$ and $(w_n)_{c-r}$ are the non-evaporable water contents of plain cement paste, replacement material, and due to the enhancement in cement hydration from the presence of the replacement material respectively, and m_c and m_r are the mass fractions of the cement and replacement material respectively in the paste. Detailed derivation of this model and its application to selected cement pastes containing pozzolanic cement replacement materials has been reported²².

From the values of σ_{eff} and σ_{pore} , the parameter $\phi\beta$, which is the product of the pore volume fraction and pore connectivity factor, can be easily obtained. Since the porosities of the concretes before subjecting them to the NSSM test were determined using a vacuum saturation method in this study, the pore connectivity factor of the specimens prior to chloride migration can be easily isolated. However such an attempt is not made here because: (i) the porosities of the specimens after the NSSM test were not determined, and (ii) both the volume fraction and connectivity of the pore network are responsible for moisture and ionic transport, and hence they are treated as a coupled microstructural feature.

Figure 2 shows the variation of $\phi\beta$ as a function of curing duration for the plain and modified concretes. Reduction in values of $\phi\beta$ is observed with increase in curing duration for all the specimens, which provides a quantification of microstructure densification. At early ages, the fly ash modified concretes are found to have similar $\phi\beta$ values as that of plain concrete, but at later ages, when the pozzolanic reaction of fly ash begins, the $\phi\beta$ values of those mixtures are found to be lower. The $\phi\beta$ values of silica fume modified concretes are only about half of the values of the plain concrete, showing the increased microstructural densification in these mixtures. The use of σ_{eff} values along with the pore solution conductivities is seen to provide a reliable means of quantification of microstructural changes as function of curing duration.

The relationship between $\phi\beta$ before the tests and the RCP values of all the concrete mixtures at various curing durations is shown in Fig. 3(a). It can be observed that the $\phi\beta$ and RCP values have a very good linear correlation. This suggests that $\phi\beta$ obtained from electrical conductivity describes the microstructural feature(s) that are influential in the rapid chloride permeability test. This is expected because RCP by itself is just a conductivity (or resistivity) test²³. In order to obtain $\phi\beta$, the specimen conductivity is normalized by the pore solution conductivity (determined as described in an earlier section), and hence

the influence of any changes in the pore solution conductivity that are likely to influence the RCP values are removed. A detailed explanation of how the influence of pore solution conductivity can be accounted for in the measured RCP values of several modified concretes has been reported²⁴. The relative influence of reduction in pore solution conductivity through the use of cement replacement materials (silica fume in particular) and the pore structure refinement have been separated in this publication by the authors.

Figure 3(b) depicts the relationship between $\phi\beta$ and the non-steady state migration coefficients (D_{nssm}) of concretes. Even though a linear relationship is observed between $\phi\beta$ and D_{nssm} , it is not as strong as that observed between $\phi\beta$ and the RCP values. The points that lie towards the right hand side of the plot (the ones that does not appear to fall in the fit line) correspond to the plain and fly ash modified concretes especially at early ages. Even though the plain and fly ash modified concretes at earlier ages show higher $\phi\beta$ values (larger pore volume fraction and/or more connected pores), the D_{nssm} values are found to be lower. This can be attributed to chloride binding by the aluminate hydrates in such concretes under the conditions of NSSM test. The binding is more prominent in the case of porous microstructures where more chloride ions can penetrate. In the relationship shown in Fig. 3(a) between the RCP values and $\phi\beta$ values, such a distinction is not observed because the RCP test does not represent chloride binding²³ because of the shorter duration of the test and the lower concentration of chlorides in the catholyte cell when compared to the NSSM test carried out in accordance with NT Build 492. To confirm the formation of chloride binding products in the NSSM test, X-ray diffraction (XRD) and thermogravimetric analyses (TGA) of the paste phase of concretes were carried out. The XRD patterns of plain and fly ash modified pastes are shown in Fig. 3(c). The peak corresponding to Friedel's salt is found to be higher for the fly ash modified paste, showing higher amounts of binding with increased aluminate content in the mixtures (see Table 1 for the chemical composition of the raw materials). The mass loss corresponding to Friedel's salt from TGA was also found to be higher for the fly ash modified paste (2.0%) as compared to the plain paste (1.51%).

The discussions above show that effective conductivity can be used to extract a microstructural parameter ($\phi\beta$) that can relate to the rapid chloride transport parameters (RCP and D_{nssm} values). In the following section, an equivalent electrical circuit model based analysis is presented to evaluate the microstructural changes that occur in concretes due to chloride ingress.

Monitoring the changes in material microstructure as a result of chloride transport using electrical impedance

As described in the previous section, chloride transport under non-steady state migration tests creates changes in the material microstructure because of the formation of chloride binding products. It is important to understand the influence of chloride binding on the transport coefficients (increased binding will result in lower transport coefficients, possibly leading to the erroneous conclusion that the microstructure is denser than it actually is) and on the microstructure. For instance, Fig. 4 shows the relationship between the bulk resistances of the specimens determined using EIS before the chloride transport test, and the non-steady state migration coefficients (D_{nssm}). Two distinct relationships – one for the plain and silica fume modified concretes (mixtures with lower aluminate contents), and the other for fly ash modified concretes (mixtures with higher aluminate contents) can be noticed in this figure. For the same value of bulk resistance (implying similar microstructure ($\phi\beta$) if the pore solution conductivities are approximately the same, which is the case for plain and fly ash modified concretes), the fly ash modified concretes are found to demonstrate lower D_{nssm} values, which can be attributed to chloride binding in these mixtures. Another indication of the change in material microstructure because of the chloride ingress is the difference in the electrical impedance spectra before and after the NSSM tests as shown in Fig. 5 for a 20% fly ash modified concrete cured for 90 days. The bulk resistances (R_b) are found to be higher after the NSSM test, which could be attributed to the formation of new solid products. While a case could be made for the replacement of highly conductive OH^- ions by the less conductive Cl^- ions that result in reduced pore solution conductivity and thus increased bulk resistance, it has been shown that in the initial stages of an electro-migration test, this does not happen²⁵. On an average, the bulk resistance is about 9% higher after the migration of chloride ions²⁶.

In order to better understand the microstructural changes that occur because of chloride transport, an equivalent electrical circuit, as shown in Fig. 6(a) is used. Among several equivalent electrical circuits