SP-270—1

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 simultaniously.[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 microtomography[7] and scanning electron microscopy[8] (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 pastes[10] 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 proposed[12] 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 Scrivener[14] 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].

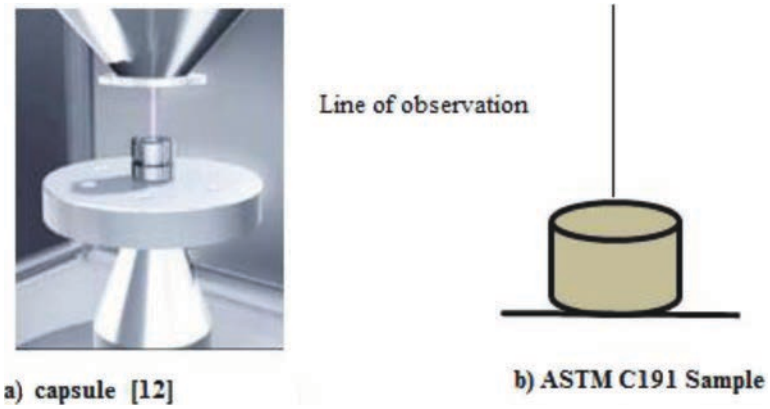

Fig. 1—Experimental samples.

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 method[15], 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

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.

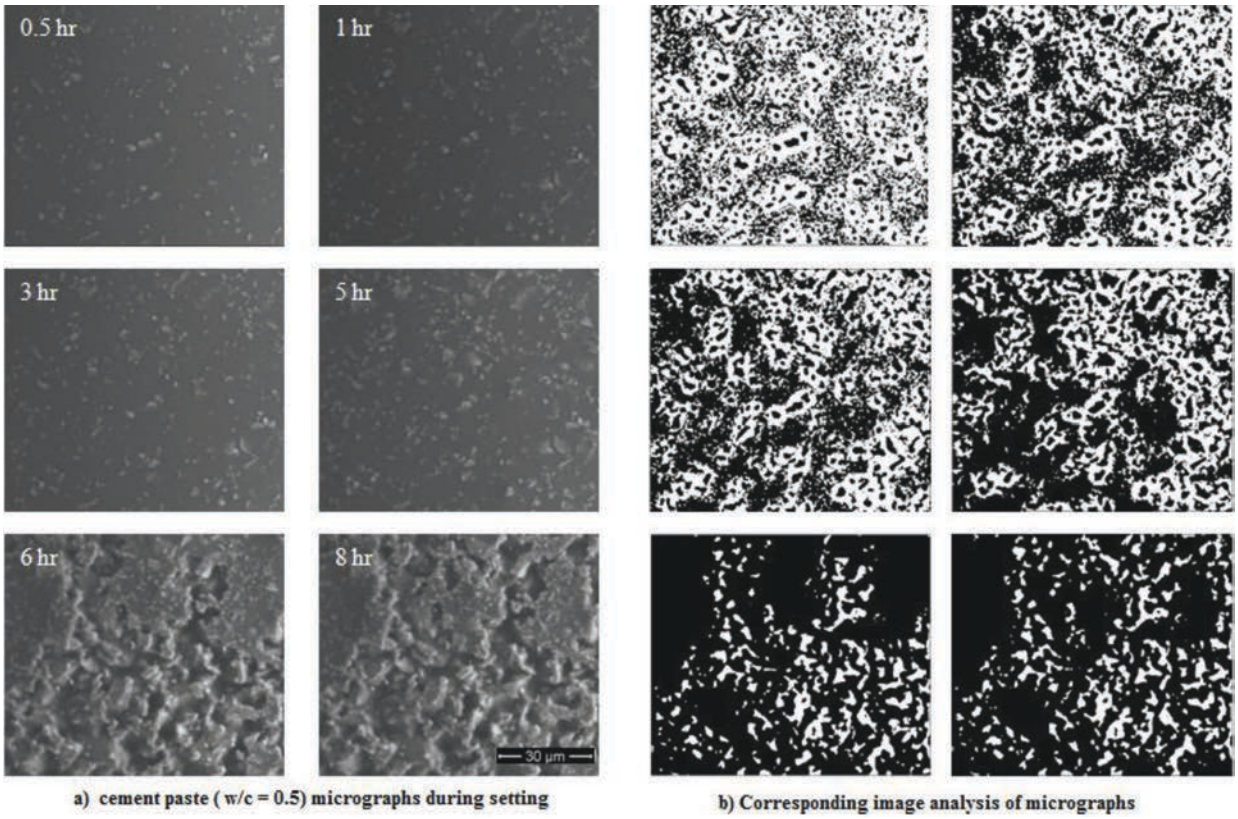

Fig. 2—Cement pastes SEM micrographs and image analysis.

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

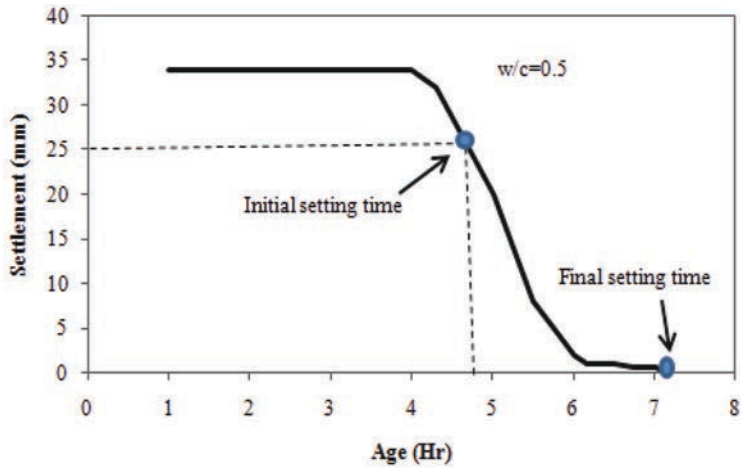

Fig. 3—Settlement of the needle during Vicat needle test. (Note: 1 mm = 0.03937 in.)

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 boundary[16]. Cement particles were classified in to three groups with the majority of particle diameter falling in the ranges of 2-5μm, 7-10μm, and 10-15μm. 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 2-5μm have increased about 25% compared to their original sizes, for the 7-10 μm size group, the average diameter is increased by 20%, while for 10-15 μm 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 rate[1]. 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 μm 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

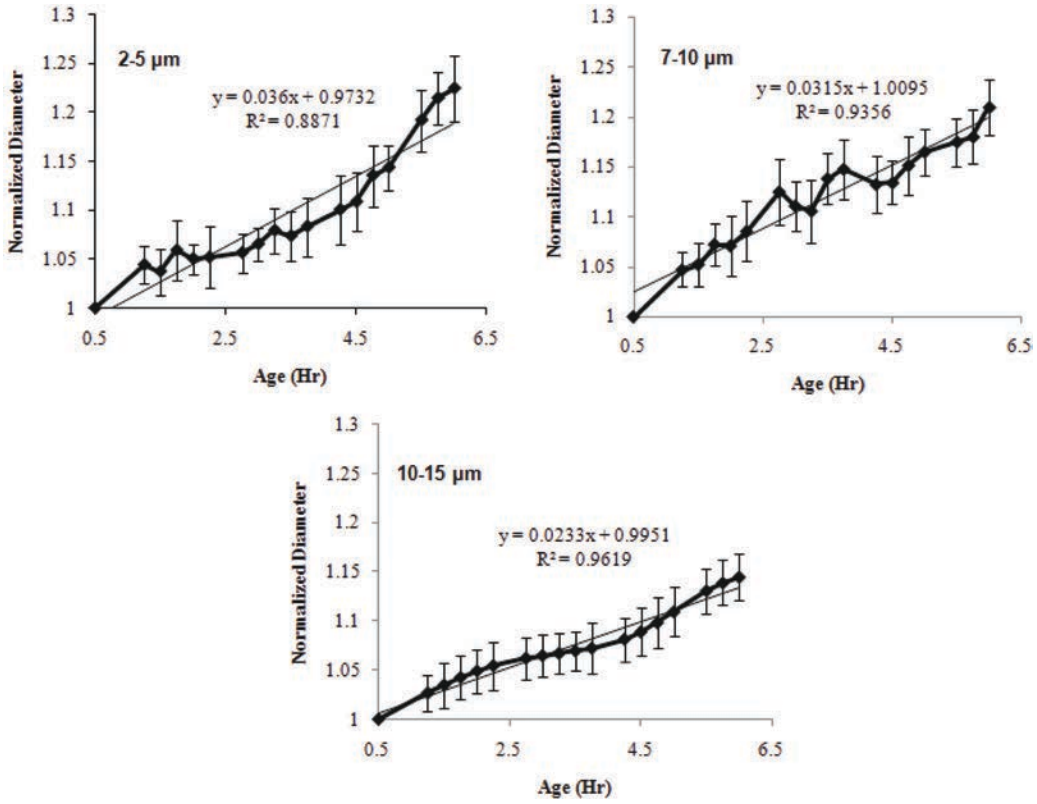

Fig. 4—Different sized particles growth.

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 rage 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 with in 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% to85%, 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,

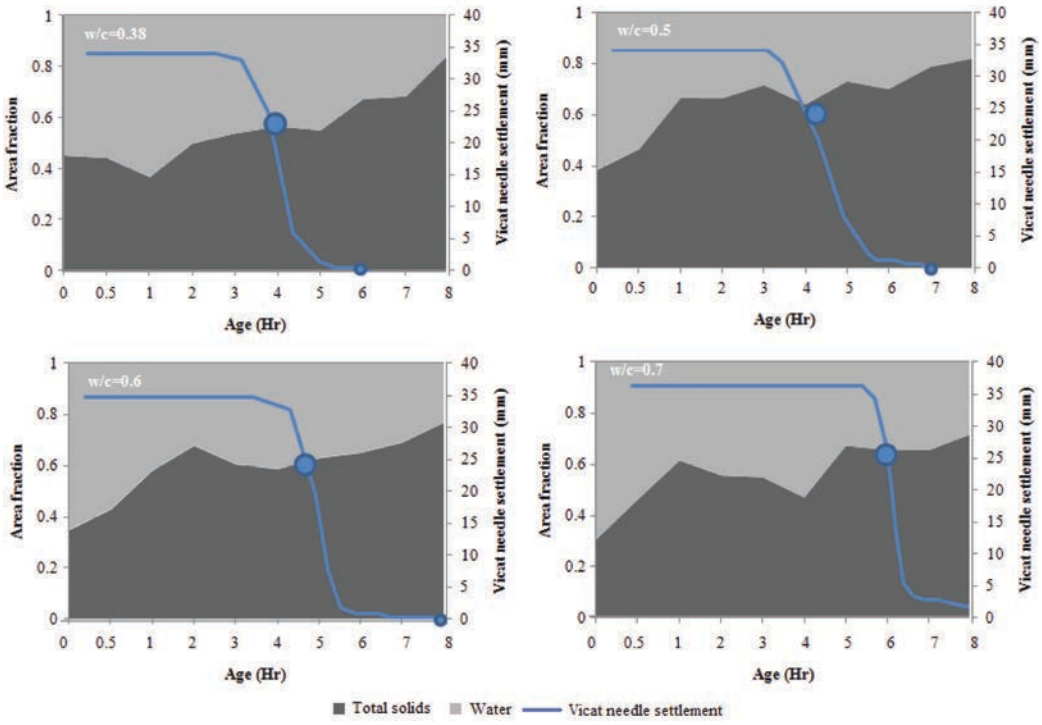

Fig. 5—Different phase developments during cement paste setting. (Note: 1 mm = 0.03937 in.)

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 seem 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.

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SP-270—2

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.