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In situ observation of cement particle growth during setting

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ABSTRACT

The evolution of the cement paste microstructure is a complex phenomenon, which governs the setting of concrete. During setting, cement particles tend to flocculate and agglomerate due to their surface charges, attraction forces and variety of other reasons. However, it is still unclear how these developments in cement paste microstructure influence the setting of concrete. In order to better understanding the correlation between cement paste microstructure development and corresponding concrete behavior during setting, in situ observations on cement particles behaviors are essential. In this study, in situ observations on microstructure development of fresh pastes were made on three different cement pastes by using a newly developed Quantomix WETSEM™ capsuling system in a conventional scanning electron microscope. Further, by employing image analysis techniques on the captured images, microstructure changes of these cement pastes were investigated quantitatively. During the study single and multiple particle growth, hydration rate of different cement particles, and total solids growth in association with various solid concentrations and corresponding heat of hydration were studied quantitatively and as well as qualitatively. The purpose of this quantitative study is to investigate the feasibility of using such a new technology to evaluate the factors influencing the cement paste microstructure evolutions during setting.

1. Introduction

Concrete is a mixture of Portland cement, water, aggregates and in some cases admixtures. When cement powder is mixed with water, a series of chemical and physical changes happen due to the hydration of cement. During this process the cement paste stiffens gradually and bonds the aggregates together to make a solid concrete skeleton. This stiffening behavior of cement paste in concrete is known as setting [1]. Cement paste setting is a complex phenomenon of cement particle dissolution, precipitation, agglomeration, diffusion and a variety of chemical reactions, and further it is a short period process compared to lifelong process of hydration. In this period, chemical, physical and mechanical properties of concrete undergo rapid change, which may also have the influence on concrete quality and life time performance. In practice, concrete setting time is a crucial parameter during scheduling of different events in construction, because once concrete sets, it is impossible to remix, replace or alter the original concrete mass. Thus an accurate estimation of setting behavior of cement pastes is essential for better understanding of the fresh concrete setting.

As stated above the setting behavior of concrete is governed by evolving microstructure in its cement paste. The evolving microstructure depends on solid dispersion (cement powder), which is a function of particle shape and size distribution, particle packing, solid concentration and surface and pore solution chemistry [2,3]. Due to the cement particle flocculation and agglomeration, size distribution, interaction (forces between the particles) and variety of other reasons, an ideal dispersion can never be achieved in practice. It is still unclear how and up to what extent particle flocculation affects the setting. Current methods, such as Vicat needle method [1], ultrasonic wave method [4], and electric resistivity method [5] are limited to macro properties, and fail to give insight information on cement paste microstructure evolution during setting.

Researchers are using imaging methods, such as neutron scanning [6], soft X-ray [7,8], and X-ray microtomography [9] to observe the developments in microstructures of cement-based materials. Among the various imaging techniques, scanning electron microscopy (SEM) [10] is commonly used. In this technique, backscattered electron (BSE) and secondary electron (SE) detectors are used to image the different compositions and topography of materials, respectively. SEM-BSE mode has been used widely to study the mineralogy of clinker and cement powder [11], the hydration process of cement pastes [12], and the microstructure of cement pastes in hardened concrete [13]. All the SEM experiments require samples in solid state with sample preparation processes like drying, freezing, resin coatings, etc. Although the environmental SEM (ESEM) is suitable for wet samples, ambient

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temperature changes (during the hydration) limit the usage in wet cement pastes. In general due to their tedious sample preparation processes and testing conditions, the applications of SEM are limited to hardened concretes.

A new sample preparation process, WETSEM™ technology, was proposed for cement-based materials by Quantomix [14], which was originally developed for observing live cells. Using this technique, without the need of above mentioned sample preparation processes, wet samples can be placed directly into a capsuling system and imaged in a SEM. Katz et al. [15] conducted preliminary studies on this technique to investigate the hydration of gypsum and cement. It was reported that using this capsule, it can be possible to have observations on microstructure of fresh cement paste right after mixing with different magnifications in a conventional SEM. It was also found that it can be possible to see both C–S–H and CH around cement particles and the formation of crystalline forms of hydration products during cement paste hydration. Furthermore, Gallucci and Scrivener [16] 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 convenience of sample preparation process, and the capability of studying the hydration of cement-based materials dynamically. However, wall effect was reported due to the vacuum tight membrane of this capsule. It was found that smaller particles tend to accumulate near the membrane. Although dynamic in situ observations of cement pastes have been conducted, no quantitative study on particle growth with this technology has been reported. Further, if this kind of technology is used in understanding the physical changes in microstructure, i.e. particle growth, agglomeration and flocculation, a better understanding of the setting behaviors in cement pastes becomes possible.

The objective of this research is to make quantitative and as well as qualitative studies on cement paste microstructures developments, and to understand the physical growth in cement particles during setting. In this study, using Quantomix capsuling system, all the SEM observations were made continuously on three different plain cement pastes with water-to-cement (w/c) ratio varies from 0.5 to 0.7 up to 8 h after mixing. Further, by using image analysis techniques on SEM images that were captured, features in microstructures were studied. During the study, single and multiple cement particle growth, hydration rate of different sized cement particles, water and solid volume fraction changes and correlations between total solids growth and heat of hydration were studied quantitatively.

2. Experimental study

2.1. Materials and sample preparation

In this study plain cement pastes with water-to-cement (w/c) ratios equal to 0.5, 0.6 and 0.7 were prepared using ordinary type I Portland cement and tap water. Quantomix QX-202C capsules were used in sample preparation process of SEM imaging as shown in Fig. 1. A typical capsule contains a sample holder in which cement paste can be placed inside and imaged outside via membrane. Further, moisture loss can be prevented in cement pastes by simply closing the sample holder with a rubber sealing stud.

During the sample preparation process, cement powders were firstly hand mixed with water for about 3–4 min. The paste was then transferred into sample holder and sealed with rubber seal as shown in Fig. 1. This process took about 1 min, and the capsule was then placed in SEM chamber (as capsule membrane facing the electron beam) for imaging. Having the advantage of a grid system on the capsule membrane, it can be possible to track an exact location of a specific area of cement paste microstructure during the observations. The detail image acquisition and analysis procedures are described in the following sections.

2.2. SEM image acquisition

Nova Nano SEM 600 was used for capsule imaging with observations being conducted at 20 kV and working distance of 7.5–8.5 mm. During the SEM observations, if electron beam is focused on a particular region for a long time, there is a possibility of generating extra heat, which may modify the hydration kinetics, the microstructure development, and also damage the capsule membrane. Hence, to prevent the damage and leakage, beam blank option in SEM was used to facilitate the continuous observations of cement paste. In this work, all SEM micrographs were captured by using BSE detector at magnification of 800× with the same contrast, brightness, and chamber temperature. Further, for each given paste, images of a same area were taken up to 8 h after mixing with a time interval of 15 min. In order to account for the statistical variations, three experiments for each w/c ratio were conducted along with observations of five grids for a particular time interval in each experiment. Since the cement pastes were prepared by hand mixing, in some capsule membrane grids, particles were unevenly distributed. In this regard for better representation of the bulk cement paste, prior selection of grids was made with more or less evenly dispersed cement particles. Representative SEM-BSE micrographs

Fig. 1. Quantomix-202C capsule.

of three mixtures at the age 30 min after mixing are shown in Fig. 2.

2.3. SEM image quantification

Based on the scope of this paper, image analysis technique was employed on basic material growths during cement pastes microstructure evolution, i.e. cement particles and water. An automatic image analysis software was employed to measure the growth of each cement particle, and also to quantify the two phases: water and solids. The features in SEM images were distinguished by using a threshold method [17], which is based on gray level histogram of the image. During the analysis, a histogram was generated by the software based on the gray level value of each pixel in the processed image. A binary segmentation was then applied to pixels of a particular gray level value by using the generated histogram. Area fractions of both phases (water and solids) in binary image were then estimated by choosing areas represented in black or white color (Fig. 3). Thus, selection of a reasonable accurate thresholding value for corresponding feature (water or solid) in SEM image analysis is very important. However, in early-age SEM images, gray levels of water and solids are continuously changing due to the rapid progression of cement paste hydration, which intern complicates the process of fixing a gray level value. This is also indicates that the image analysis process should be done in different way than hardened cementitious materials. In this study, the physical development of two phases in the microstructure of the paste was traced by fixing a gray level value for water. Since, the brightness and the contrast were kept constant during the imaging processes, the gray level of initial water should not change during the whole process. However, due to the overlapping of gray values, it is also a very difficult task to distinguish exact gray levels for different waters in fresh cement paste. In order to overcome this situation, a new approach was used based on the variations in pixel gray values of various cement pastes SEM images at age 15–25 min by assuming that the majority of water molecules are not contributed in hydration during this short period. In these images, especially gray values of areas such as where there is no particle and areas around the cement particles were studied. Form the observations, a gray value 45 of these areas was then fixed for water (i.e. water is 45 or less and total solids are greater than 45 on a 255 scale), area fractions of solids were then estimated for each time interval by measuring the areas above this gray value in binary image. Based on the Stereological principles [18], these 2-D area fractions can be approximately related to 3-D volume fractions of relative phases [12,19,20]. Fig. 3 shows the binary segmentation using threshold method, and features in black and white represent total solids and water, respectively.

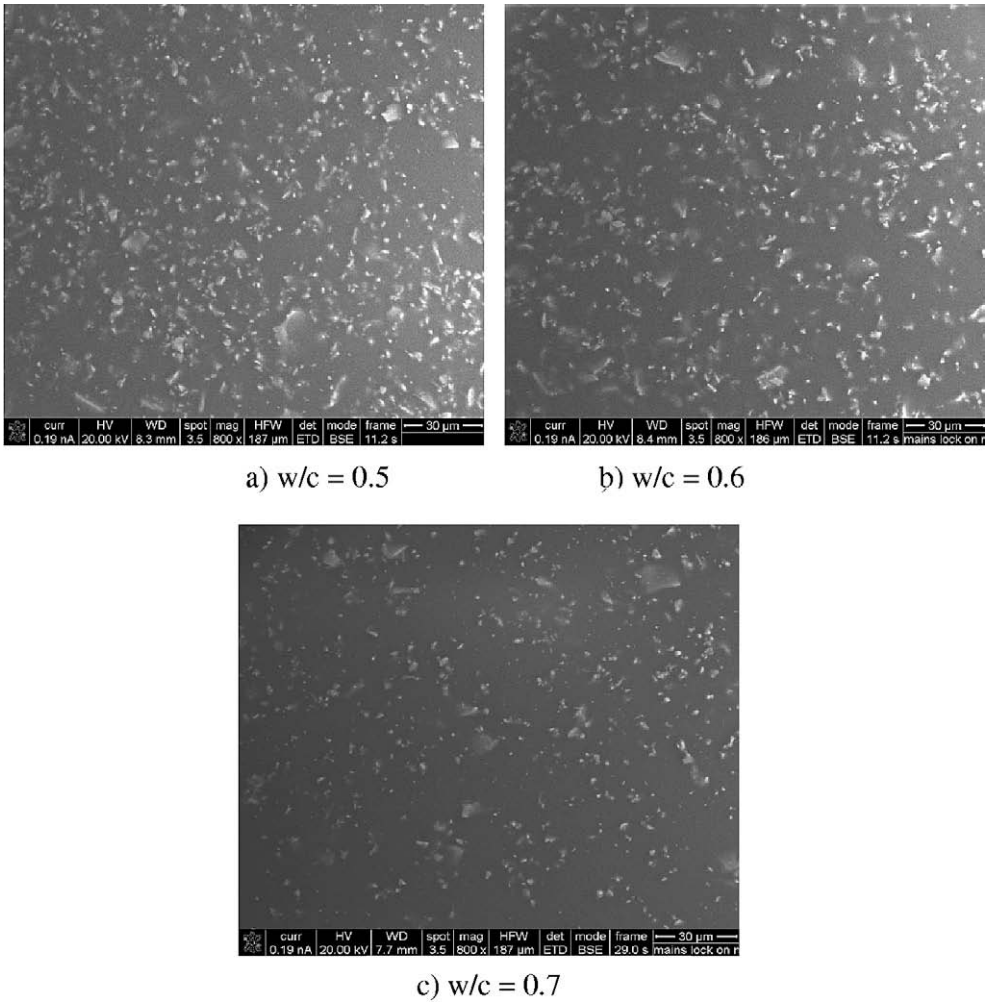

Fig. 2. Cement pastes micrographs at age 30 min.

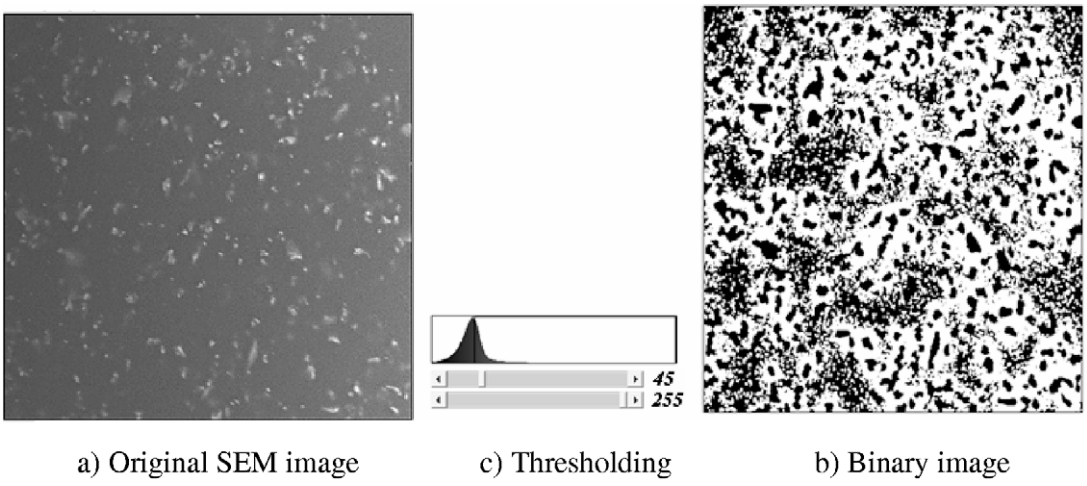

Fig. 3. Image analysis of total solids.

3. Results and discussion

3.1. Cement particles growth

The change in individual cement particle diameter with time was measured to investigate the growth of cement particle. Here, a cement particle diameter is represent by Feret's diameter, which is defined as the longest possible distance between any two points along the selection boundary [17]. A particular particle was selected from the initial micrograph, and this particle was then analyzed up to 6 h after mixing by using the introduced threshold technique as shown in Fig. 4. In the present work, cement particles were classified into three groups with the majority of particle diameters falling in the ranges of 2–5 μm, 7–10 μm, and

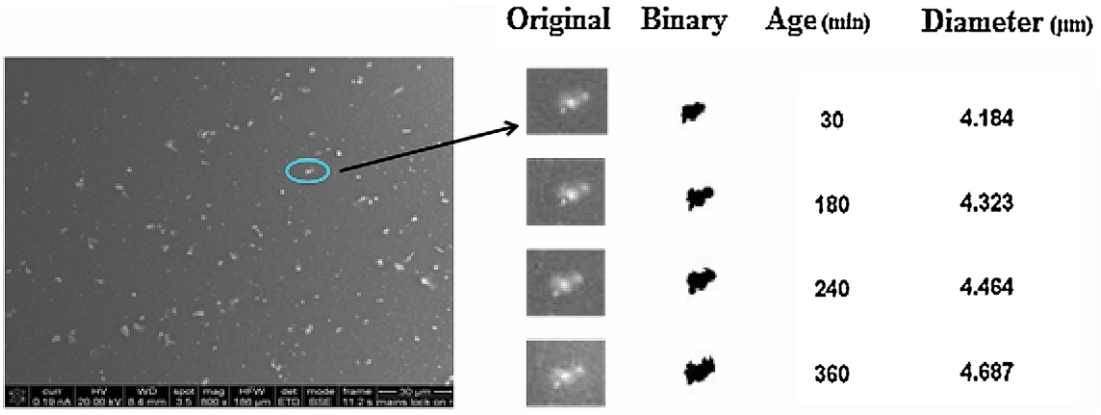

Fig. 4. Single particle image analysis.

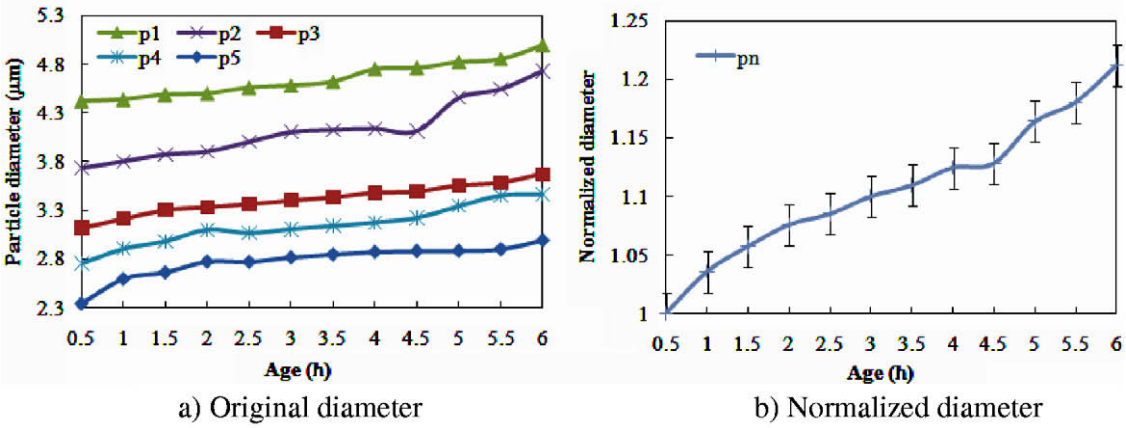

Fig. 5. Cement particles growth in 2–5 μm particle group.

10–15 μm. Some of the particles growth (p1, p2, p3, p4 and p5) in 2–5 μm group are shown in Fig. 5a. From the figure, it can be observed that as the hydration age is progressing particle diameter is increasing. However this increase seems to be more at very early ages (up to 3 h) compared to later ages (3–6 h). It was also observed that some of the particles (example: p2) do not exhibit smooth growth patterns. The reason for this kind of growth in particles can be attributed to the change in orientation of particle during the dynamic progression of early hydration.

To compare the growth rates among these three different size particles during hydration, for each group, normalized diameter for each particle was measured with its original diameter (Fig. 5a) and then for all the particles normalized diameters were averaged as shown in Fig. 5b. For the total 30 particles in each size group that were analyzed, the normalized average sizes and corresponding linear regressions are as shown in Fig. 6. It shows that 6 h after mixing, particles with diameters of 2–5 μm 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 linear regression also shows (Fig. 6), irrespective of w/c ratios, smaller particle's growth rate (slope of the linear regression line) is higher compare to larger particle's. Here, the slope of 2–5 μm (0.036) > 7–10 μm (0.0315) > 10–15 μm (0.0233). The reason for this high growth rates in smaller particles is due to the larger surface area to volume ratio, which helps to enhance the hydration rate [1]. It was observed that due to the less surface orientation changes during the hydration process, 10–15 μm group particles exhibited steady growth rate (less scattered data points in Fig. 6c) compared to other group particles.

3.2. Volume fraction growth

During early age, volume fraction changes in water and solid phases are indicative of cement paste microstructure evolution. Fig. 7 shows the area fractions of water and total solids in different cement pastes at various ages. As stated above, 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 was calculated based on w/c ratio and the specific gravity of cement powder (0 h in Fig. 7). The authors also tried to measure the area fractions of cement particles from the obtained SEM images at age of 15 min after mixing by assuming hydration does not increase the solid volume significantly during the first 15 min. It was found that most of the time, the volume fraction of solid phase obtained with these two different methods match, however, sometimes SEM image analysis can lead to a lower solid fraction due to the wall effect and also settlement of cement powders. To keep the consistency, the calculated theoretical volume fractions of cement particles were adopted as the original solid area fractions. Due to the observations made in 2-D sections rather than on 3-D volumes in SEM, and the inclusion of chemically combined water (which is not fall within the range of a gray level 45 for water), the area fractions of solids are slightly different from the theoretical values. Here the total solids area fraction includes C–S–H, CH crystals, unhydrated cement, chemically combined water and fine pores within the particle. By comparing the area fractions of each phase right after mixing and 8 h after mixing, it can be noticed that for all these three pastes, the water volume is reducing and the volume of solids is increasing with the age. However, this growth pattern contradicts at the ages 4, 3, and 2 h for w/c ratios of

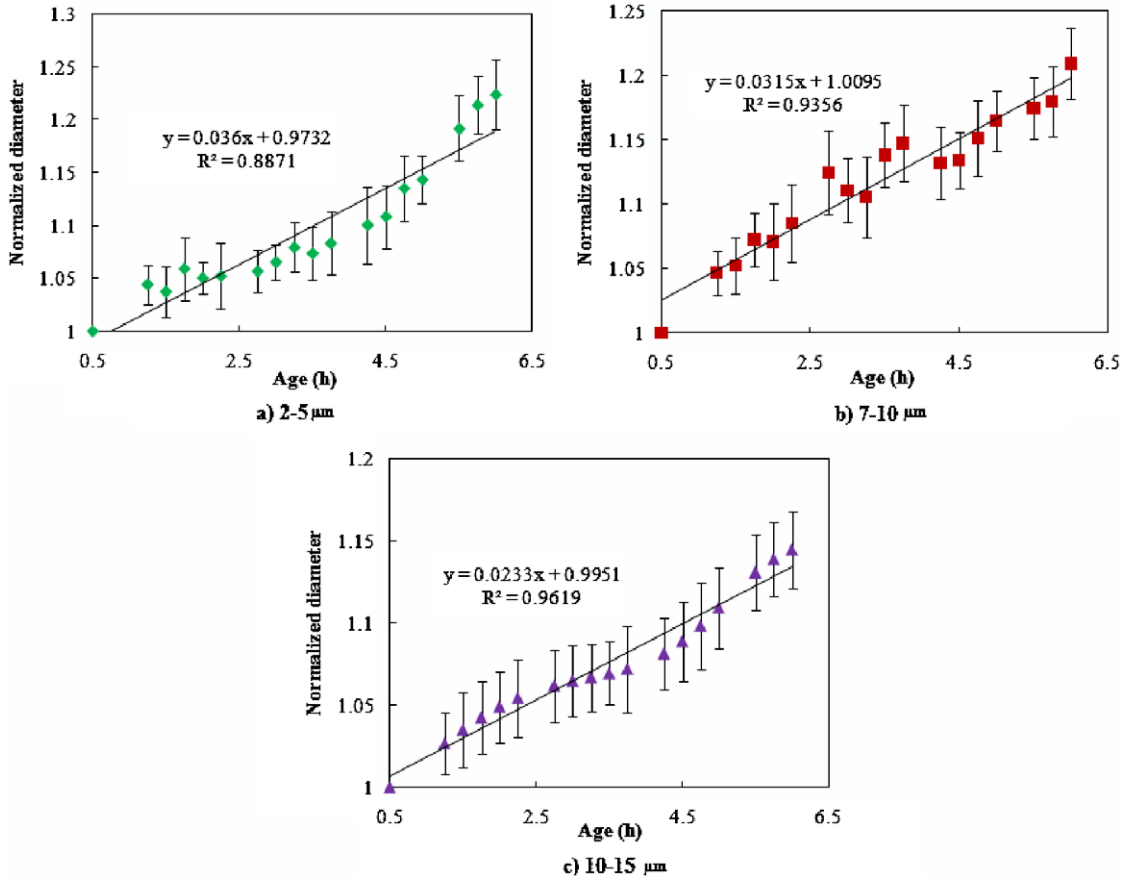

Fig. 6. Linear regression of particles growth.

0.5, 0.6, and 0.7, respectively. These changes might be due to the particles settlement, and the change in particles orientation. From the figure, it can be noticed that the area fractions of solid phase change from 38.46% to 82%, 35% to 77% and 30.86% to 74% for pastes with w/c ratio 0.5, 0.6 and 0.7, respectively. It can be observed from these area fractions changing limits that the amount of the solid phase evolutional is based on the mix proportion (richness of the mixture), i.e. lower the w/c ratio higher is the amount of final area fraction, which was true in macro level [1]. However, higher w/c ratio mixtures exhibit larger hydration rates, which can be observed from comparing the growth percentage in initial solid area fraction from that of final area fraction (113%, 120% and 140% for w/c = 0.5, 0.6 and 0.7, respectively).

3.3. Correlating volume fraction change and heat evolution

At the same SEM testing conditions, using isothermal conduction calorimetric method [1], the heat of hydration in three pastes were measured. During the test, three specimens for each w/c ratio were prepared and heat of hydration was measured by observing the heat flow from the specimen. A correlation between hydration heat evolution and total solid phase evolution for each mixture was developed as shown in Fig. 8. It can be seen from error bars that the difference in evolution patterns between heat and microstructure of cement products is less for w/c ratio 0.7 (as in Fig. 8c). This is due to the less intensity of cement particles in mixture and moreover hydration is dominating from that of physical changes. The exact reverse situation can be seen from Fig. 8a, which is for w/c ratio 0.5. A better correlation can be possible between normalized total solid phase and heat of hydration evolution as shown in Fig. 9. Here, area fractions are normalized using the original area fraction. From the figure, it can be noticed that this correlation is independent of w/c ratio.

3.4. Prediction of initial setting time at microstructural level

Initial setting times of three pastes were also measured by using Vicat needle method [21], these setting times are, 6 h for w/c = 0.7, 5.25 h for w/c = 0.6 and 4.5 h for w/c = 0.5, under 23 °C and 100% humidity (sealed) conditions. These setting times are shown in Fig. 10 by solid asterisk dot. The water phase depletion profiles of three pastes were then plotted on same figure to observe the status of water at initial setting. It can be observed that by the time of initial setting, about half of the corresponding original mixing water is consumed by hydration for all the studied cement pastes. Thus, this change (half of its original value) in initial water content can help to estimate the initial setting time at microstructural level for cement pastes.

4. Conclusions

The following conclusions have been drawn from this study:

1. Using the Quantomix capsuling system, physical changes in the microstructure of fresh cement pastes can also be studied easily, which include growth of particles and different phases.
2. In general, based on the image analysis of a single particle, an increment of 14–25% in cement particle diameter is observed at 6 h age after mixing the cement paste.

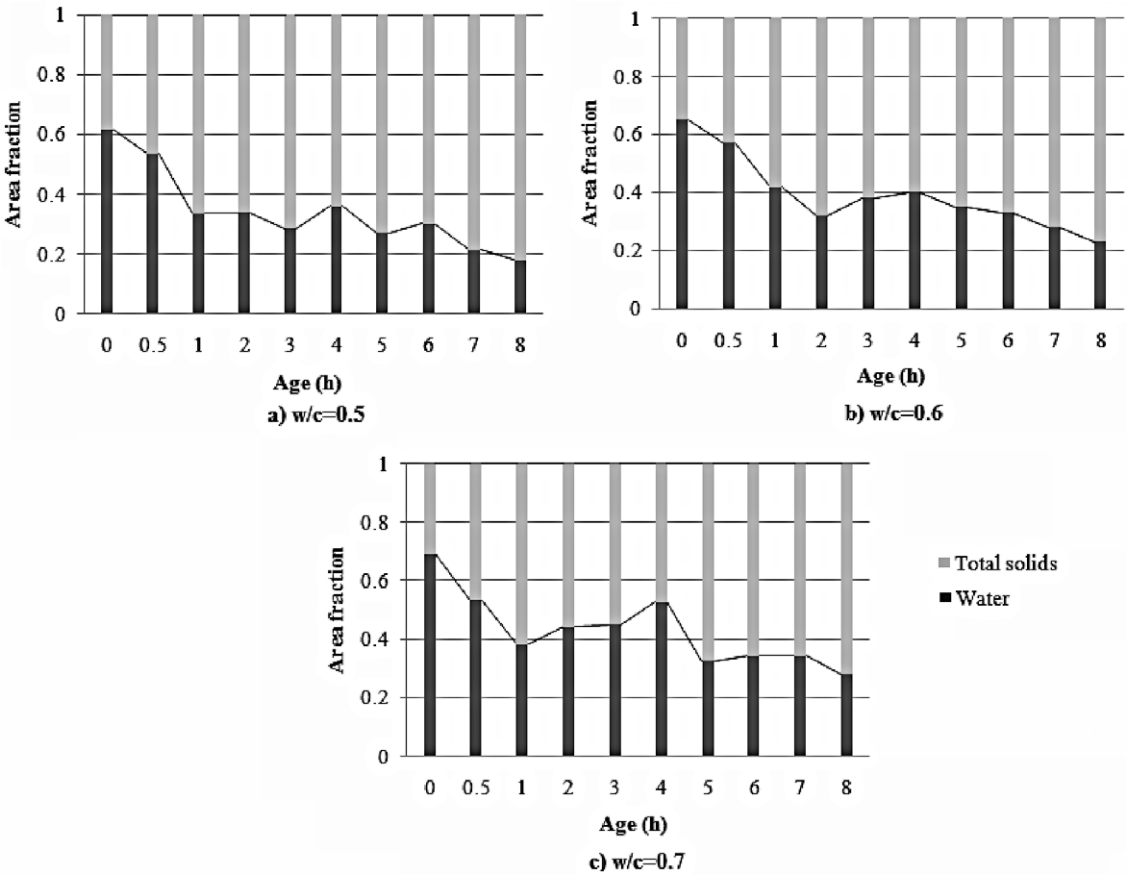

Fig. 7. Area fraction growth of different cement pastes.

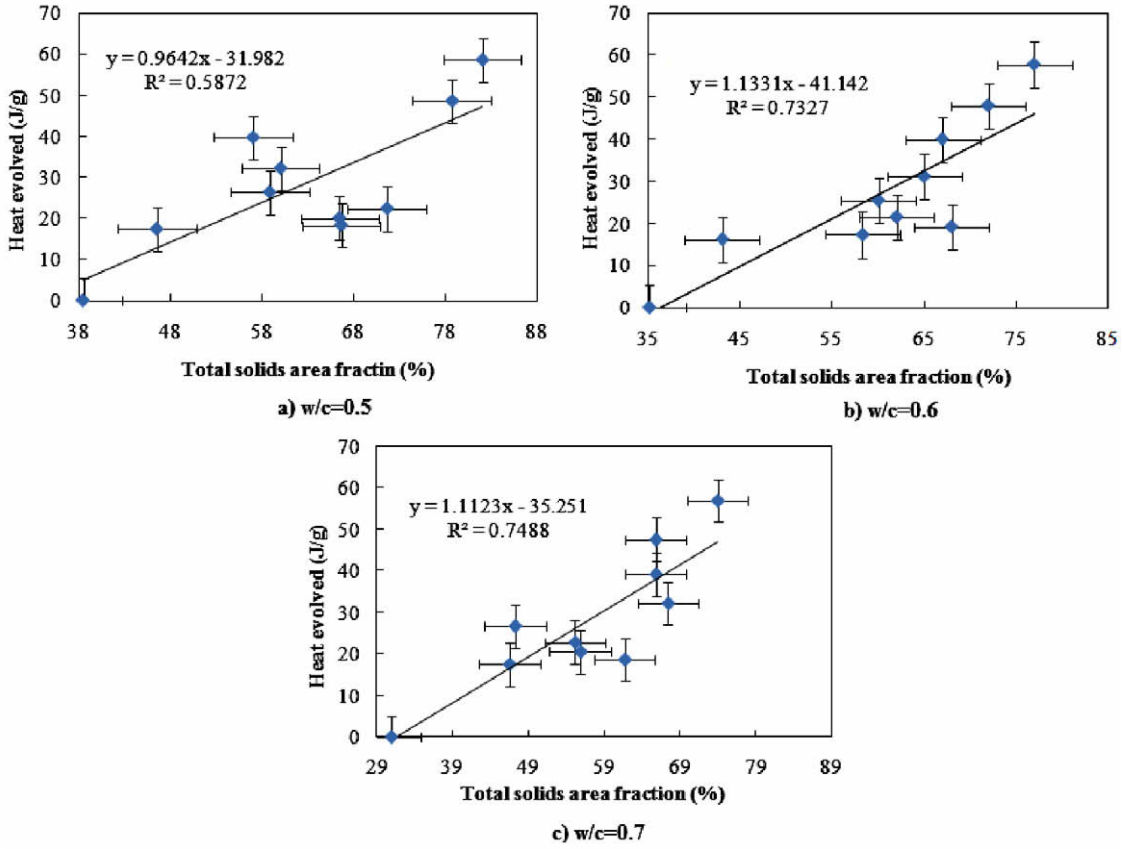

Fig. 8. Heat vs. total solids area fraction for three mixtures.

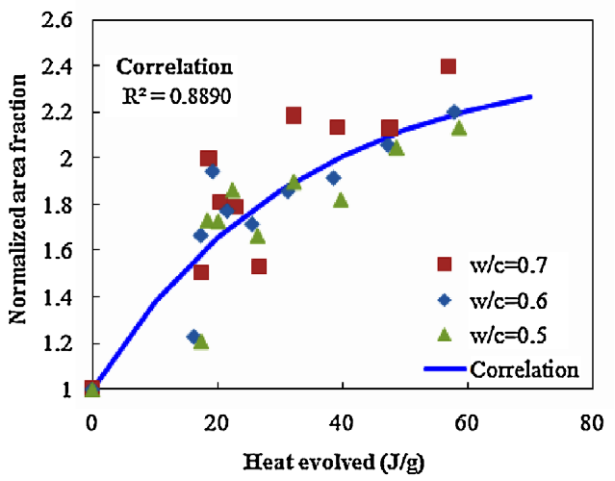

Fig. 9. Correlation between total solid phase and heat evolution.

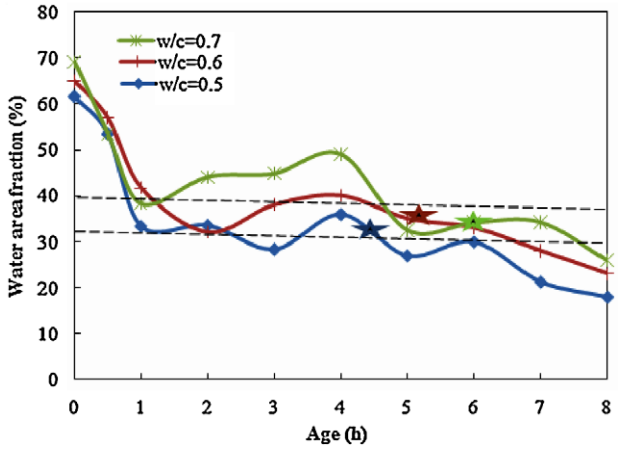

Fig. 10. Prediction of initial setting time at microstructure level based on water phase.

3. The theoretical aspects of cement particle hydration such as faster growth rate of smaller particles compared to larger particles and the larger solid volume fractions in lower w/c ratio mixtures are also observed at the microstructure level for cement pastes.
4. Final area fraction of total solids in each cement paste depends on the hydration rate of the cement particles. It is observed that final area fraction of total solids is 2.13, 2.2, and 2.4 times the corresponding initial area fraction of cement paste prepared with w/c = 0.5, 0.6, and 0.7, respectively, at 8 h after mixing.
5. The correlation between total solids area fraction and heat evolution indirectly shows the relationship between physical and chemical changes in cement pastes at the microstructure level, which is independent of w/c ratio and it can be made more reliable by introducing admixture data.
6. For all the studied cement pastes, at the time of initial setting, approximately 50% reduction in their original water content is observed, which can be helpful in the prediction of initial setting time of a fresh cement paste at the microstructural level.
7. Finally, it is necessary to observe the formations of C–S–H and CH, unhydrated cement and the formation of pores during fresh cement paste microstructure evolution, for better understanding

the complex phenomena of concrete setting and hydration. Future work of this research will focus on studying cement particle agglomeration and flocculation, the influence of admixtures on the evolution cement paste microstructure, and the relationships of initial and final setting times of cement paste to its microstructure properties.

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