ESEM DRYING TESTS: MICROCRACKING INITIATION IN THIN CEMENT PASTE DUE TO EARLY AGE DRYING

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Abstract

Scattered and discontinues microcracking as a subsequent side-effect of deformations due to early age drying, occurs in thin (approximately 1 mm thick) cement paste samples, when stepwise dried in ESEM. Microcracking of cement paste and restrains appear to be practically unavoidable. They are related to a phenomenon of interfaces (‘matrix’ and ‘inclusion’), which exists at every scale. The combined effects of sample age, curing conditions and w/c ratio, influence development of microstructure at an early age as well as appearance of microcracks and their width (0.1-2.5 µm). However, rapid change of environmental conditions in cycles of drying-wetting induces full fracture of thin cement paste samples, regardless of the mentioned effects.

1. INTRODUCTION

The new type of tests with improved experimental techniques in Environmental Scanning Electron Microscope (ESEM) are performed in order to investigate the (shrinkage) behaviour of cement-based samples when exposed to an early age drying [1-3]. The goal was determination of coefficient of (shrinkage) deformations based on drying of thin samples [3]. The coefficient would be later on used as an input parameter in the coupled numerical analysis [4, 5]. The drying of thin samples with a gradual reduction of relative humidity (RH) in ESEM should enable a determination of ‘real’ (unrestrained) deformations [6-8]. In that way, ‘apparent mechanisms’ (moisture gradient, cracking) would be avoided. This paper shows how local microcracks (size <10 µm) and even severe cracking may emerge in thin cement paste samples under variable environmental conditions.

2. NEW METHOD OF SAMPLE PREPARATION AND DRYING IN ESEM

The neat cement (CEM I 32.5 R) paste samples are cast directly in a small size and low thickness (10 x 10 x 2 mm) in a specially developed mould [1, 2]. After wet or dry curing the sample thickness is reduced by a careful grinding and polishing with a specially designed tool [1, 3] to about 1 mm (Fig. 1a). A special cooling stage is designed for ESEM (XL30) chamber to enable thin sample drying (Fig. 1b). The drying conditions inside the chamber are created with a reduction of RH. The temperature is kept constant (9-10°C), while pressure is reduced...
from 9.1 torr to 1.8 torr stepwise by 2 (or 1) torr. In this way a gradual drying is performed from 100% to 20% RH by the step of 20% (or 10%) RH respectively. The reduction of RH is performed every time the moisture is equilibrated i.e. when pressure and temperature variations diminish. The drying time interval prior to moisture equilibrium, depended on the sample age, w/c ratio and curing conditions. It also depended on the RH: being longer at higher RH and shorter at lower RH. In average, it varied between 15-20 min. The acquiring of images is performed by means of GSE detector approximately in a middle of the specimen at each drying step. The drying below 20% RH (pressure below 1.8 torr) often resulted in blurry images. The blurry images were not considered in the image analysis. The deformations (shrinkage or expansion) are determined by means of digital imaging (Vic-2D code) in the center of every pixel. The average values of deformations are calculated as a function of RH.

Several effects may influence drying shrinkage deformations, but also the compressive strength and microcracking. The following effects are considered in these tests: age (from 2 to 52 days; curing age equals sample age prior to testing), w/c ratio (0.5 and 0.3) and curing conditions (wet or dry-sealed). Here are presented results of two groups of the ESEM drying tests: (1) drying of 1 mm thick cement paste samples and (2) drying of 1.1-1.2 mm thick cement paste samples. The samples in the group (2) were alternately exposed to the cycles of drying-wetting (or vice-versa) conditions, depending on the way of curing.

3. MICROCRACKS DUE TO FIRST DRYING (GROUP 1 SAMPLES)

Effect of age in wet cured samples. Microcracks occurred randomly on the sample surface, starting from the age of 4 (Fig. 2a) to the age of 52 days (Fig. 2b). Lack of microcracks by age of 4 days is probably related to the relatively ‘elastic’ cement-based microstructure. In the 4-day old sample, the microcrack (width ~ 2.5 µm) is observed (Fig. 2a). The short 15-min rewetting to 80% RH performed after drying, showed the partial healing and irreversible shrinkage, which was similar to the behaviour of 5-day old paste. Microcrack width reduced in time from 2.5 µm (age 4 days) to 2 µm (in 30 days) and 1 µm (52 days), (Fig. 2b), together
Figure 2. Microcracking in wet cured cement paste (CEM I 32.5 R, w/c 0.5): (a) age 4 days at 20% RH and 20 μm; max average shrinkage (ε_{yy}) reached (-0.2) in large AOI; (b) age 52 days, at 20% RH and 5 μm; max average shrinkage (ε_{xx}) reached (-0.003) in large AOI.

with strains. The moisture was equilibrated much quicker in older samples than in young samples. In the case of young samples, the time interval between two adjacent RH values was about 15 min, which was expectedly longer (approximately double) in comparison to the time intervals of older samples. The nondestructively determined moisture-induced plane strains appeared orthotropic for all samples. They were reduced by aging and after drying to 20% RH. The strain distribution in all samples showed the localized highest shrinkage (expansion) strains but with the variation (decrease) in values, depending on the age. When the ESEM images are analyzed by the digital image analysis of large (1334 x 878 pixels) and/or small (209 x 202 pixels) Area-Of-Interest (AOI), the local linear or shear strains (ε_{xx}, ε_{yy} and ε_{xy}) were found to vary from one local AOI to the other. It was found that the strain distribution typically depended on the chosen AOI, its size and the strain direction (x-x, y-y or x-y). An example of strain distribution (ε_{yy}) in 4-day sample is shown at 30% RH presumably prior to the microcracking (Fig. 3). The two small AOIs are arbitrarily chosen at different locations. The strain distributions and the extreme strains vary depending on the AOI location (Fig. 3).

Microcracks rarely occurred in the chosen middle part of the samples observed under the ESEM. Due to the ESEM technique constrains, it was not possible to detect the exact RH and the moment at which microcracking occurred during testing. The RH at which microcracks occurred could be speculated to vary between 30%-40% RH, based on the average strain calculations from the Vic-2D analysis of large AOI. Also, the variations in contrast and brightness in the images during the RH-decrease, play a role. They could be closely related to the transport of water vapour. These variations in moisture probably influence the properties of cement paste from micro-level to even atomic bonds.

Microcracks emerge due to inner local restraints in a complex cement paste microstructure. It could be assumed that microcracks in samples (age 4 to 30 days) occur due to the large presence of CH crystals and ettringite needles that bridge the pores. Ettringite forms as the initial hydration products, but dominates over C-S-H formation up to 30 days. Brown [9] observed that ettringite needles continued its growth while creating critical tensile stresses on pore walls, which probably initiated early cracking. Ettringite tends to disappear in time; at 30 days of age ettringite needles cannot be found [10]. The microstructure contains then mostly C-S-H in which ‘restrains’ are embedded, such as CH hexagonal crystals and monosulphate.
Figure 3. Strain distribution ($\varepsilon_{yy}$) in 4-day old sample in two small arbitrarily chosen AOIs, size (209 x 202) pixels at 30% RH. Total area observed under the beam is (1424 x 968) pixels or (280 x 180) µm; scale bar = 50 µm. Max shrinkage strains: (a) (-0.499) and (b) (-0.169). They contribute to microcracking already after 3 days of age. Probably CH takes over the restraining role in the cement microstructure after 28-30 days, but less actively compared to ettringite. Additional contribution to microcracking comes from the mutual restraints in the C-S-H, i.e. between outer low-density (LD) and inner high-density (HD) C-S-H [11, 12].

Effect of w/c ratio (0.5 and 0.3) in wet cured samples. The microcracks in wet cured samples are influenced by the variations of w/c ratio, besides aging. While reduction of RH below 40% induced microcracks in the samples with w/c 0.5 at all ages (Fig. 4a), microcracks in cement pastes (w/c 0.3) were not found during drying. An average drying time interval in samples with w/c 0.3 was about 25 min and around 10 min for the samples with w/c 0.5, almost regardless of the sample age. Obviously, the higher/lower w/c ratio has different influence on the growth of a microstructure.

In the 7-day old sample (w/c 0.3), random characteristic voids (max 100-200 µm in diameter) emerged isolated, probably due to air or water bubbles that remained in the bulk during curing and the break of continuity in the capillary system due to drying. With aging (in 30-day old sample), the voids substantially reduced. The comparatively uniform strain distribution with max strain (-0.001) is observed in samples with w/c 0.3. This can be compared with Pickett observations [13]: the increase of shrinkage uniformity reduces shrinkage stresses in an unrestrained specimen and, hence, reduces the tendency of spontaneous cracking. If CH and ettringite are considered to influence microcrack formation in cement paste with w/c 0.5, then the growth of CH and ettringite is probably slowed down by the lower w/c ratio. The absence of microcracks can be also attributed to a higher compressive strength, which increases with a decrease of w/c [14]. Increase in moisture content in a form of a higher w/c ratio, in wet cured cement paste sample, decreases and postpones the gain of strength, because the adsorbed water reduces specific surface energy, which is important in colloidal substances.
Figure 4. Images taken after the test show (a) microcracks in wet cured 32-day old cement paste (CEM I 32.5 R, w/c 0.5) at 30% RH and 5 µm, (b) microcrack in dry cured (sealed) 30-day old cement paste (CEM I 32.5 R, w/c 0.3) at 80% RH and 5 µm.

Effect of dry (sealed) sample curing (w/c ratio: 0.5 and 0.3). Due to the sealing conditions, the decrease of moisture content results only from the self-desiccation. The microcracking in sealed cement paste samples started to emerge after 28 days of age. W/C variations had influence on the initiation of negligible ‘splitting’ inside C-S-H in samples with w/c 0.5 and microcracks in crystallized structure in samples with lower w/c (Fig. 4b). The microcrack width was below 1 µm and varied between 0.1-0.5 µm. This is because dry curing combined with low w/c ratio and ageing, generates more brittle microstructure as the amount of CH crystals increases. Due to lowered hydration, more anhydrous cement particles and less C-S-H is present in the microstructure. That forms a structure with lowered strength especially in the case of low w/c ratio (C-S-H is considered the main factor in gaining cement paste strength). If drying shrinkage is claimed to be independent of (low-porous) CH [15], it is doubtful that observed microcracking in CH crystals is a result of shrinkage. The shrinkage (expansion)

Figure 5. Sample 1. (a) Acquired image of dry-cured 2-day cement paste (CEM I 32.5 R, w/c 0.5) at 200 µm and 11% RH. Spot located some 100 µm (x-x) and about (-1500 µm, y-y) from the sample center. (b) Microcracks (width 0.5-5 µm) are seen in the enlarged image at 10 µm at 1251 µm (x-x) and 1136 µm (y-y) from the center. (c) Sample 2. Fractured (wet-cured) sample (CEM I 32.5, w/c 0.3, 30-day old) at 100 µm. Image acquired at 80% RH after drying for 5 min, when cracking started from a void.
strain distributions are analyzed in large and small AOI during drying from 100% to 20% RH. These analyses and calculations of the average (orthotropic) strains showed the extreme local shrinkage and expansion, about 10 times higher in large AOI at 20% RH, compared to small AOIs, and regardless of w/c ratio. This confirms localized high deformations and the domination of curing conditions (wet or dry) over w/c ratio, when it comes to induction of microcracks during stepwise drying. The drying time interval for samples over 28 days of age (w/c 0.5) was in average 12 min (regardless of age), and about 20 min for w/c 0.3 samples, Fig. 4b. No data were collected for the dry (sealed) cured 0.3 samples younger than 28 days.

4. CRACKING DUE TO DRYING-WETTING CYCLES (GROUP 2 SAMPLES)

Due to a temporary ESEM instrument failure, the samples were exposed to cyclic variations of environmental conditions (drying-wetting-drying) or vice versa, depending on the initial curing. The tested cement paste samples from the above mentioned groups developed full fracture, regardless of the initial curing conditions, age, w/c ratio or drying step. For example, the full cracking was invoked in 1.2 mm thick sealed sample (w/c 0.5), 2 days old (Fig. 5a, b) and in 1.1 mm thick, wet cured sample (w/c 0.3), 30 days old (Fig. 5c).

Sample 1: The 2-day sealed sample (Fig. 5a, b), 1.2 mm thick, was rewetted to 100% RH and then stepwise dried to 10% RH. The sample swelled $\varepsilon_{yy}$, $\varepsilon_{xx}$ (0.006) and shrank $\varepsilon_{xy}$ (0.001) at 20% RH. Each drying time interval from 100% to 80%, to 60% and to 40% RH lasted about 12 min, but increased to 20 min in average, below 40% RH. Probably several microcracks emerged already at 40% RH since the drying time interval increased. Namely, it has been noticed that drying time interval increased after several microcracks or some larger crack occurred. Also, the temperature at the cracked sample surface always was lower (about 9°C), compared to 10°C, when the surface was completely without cracks. The full fracture occurred during drying to 10% RH, when the similar average shrinkage $\varepsilon_{yy}$ (-0.15) and expansion strains (0.1) occurred. The high shrinkage and expansion deformations at 20% RH appeared to be typical for samples where (micro)cracks occurred.

Sample 2: The 30-day wet cured sample (Fig. 5c), 1.1 mm thick, was dried in ESEM for a short time (about 5-10 min). The sample was then rewetted out of ESEM, in a pot with lime-water and afterward shortly dried in ESEM from 100% to 80% RH. It cracked after 5 min during second drying, allowing no time for acquiring images for the strain measurements. The cracks reached the width of about maximum 100 µm. The cyclic change of ambient conditions showed that in spite of dry curing, sample 1 (2-day old) appeared to be sufficiently elastic to endure a stepwise loss of moisture. That is probably due to the sample young age and w/c 0.5 ratio. Wet cured sample 2 (30-day old, w/c 0.3) appeared to be more brittle, with a lot of smaller voids/cavities on the surface, through which a network of microcracks and cracks developed (Fig. 5c). The voids increase in number and size as the w/c ratio decrease (similar is noticed in [16]). The cracking developed extremely quickly in wet cured 30-day old sample, probably due to a lower w/c and appearance of large number of voids as weak spots. Otherwise, it would be expected that aged cement paste microstructure and C-S-H in particular, gained higher strength to resist the cracking.

5. DISCUSSION AND CONCLUSIONS

When exposed to a stepwise drying in ESEM from 100% to 20% (10%) RH, the observed microcracking in neat cement paste appears highly localized. The microcracks are scattered
and disconnected and appear in a small percentage on the surface of thin (1 mm) unrestrained samples. The observed microcrack healing in the young (4-5 days old) wet cured samples could imply that the healing would continue if the sufficient moisture would be continuously supplied [17]. The healing of microcracks in dry cured samples, which went through the crystal structure, is questionable. Initiation of microcracks, their width and area of C-S-H or CH in which they occur, is influenced by the chemical changes in the cement paste microstructure during drying and a combination of effects (way of curing with age and w/c ratio).

Critical shrinkage (expansion) strains are localized as well. This is proved by the digital image analysis of the large and small AOIs in the images acquired during drying in ESEM. The chosen spot (size 280 x 180 µm) for the drying observations under the ESEM beam is located approximately in the middle of the squared (10 x 10 x 1 mm) sample. The limitation of the ESEM XL30 technique is that drying observations need to be strictly focused at only one chosen spot under ESEM beam, in order to make precise measurements of drying strains. Microcracks rarely emerged at that particularly observed spot. They were found further away (after the drying test), where healing took place. Thus, the calculated average shrinkage (expansion) can be considered ‘real’ i.e. without microcracking influence. Therefore, thin samples can be accepted as suitable for the determination of the ‘real’ shrinkage deformations and coefficient of deformation.

Microcracking seems to be inevitable in cement-based materials due to their complex and changeable microstructure, sensitive to moisture variations, especially at the young age. Generally, C-S-H breaks easier than CH crystallized, ordered system, since disordered structure is more inclined to fracture than a perfect crystal [18]. On the other hand, microcracking can be attributed to a phenomenon of interfaces, which exists at all scales in cement-based materials. Namely, the substance can be classified as ‘matrix’ and ‘inclusion’ at every level. At micro-level, C-S-H acts as a deformable matrix while CH, ettringite and unreacted cement particles act as ‘rigid’ inclusions. The quantitative domination of either a matrix or inclusion depends on the age and RH. Additionally, at submicro-level C-S-H is a two-phased structure, with high and low density fraction, which makes the cement paste behaviour even more complex.

Microcracking is invoked by similar mechanisms as assumed for the shrinkage phenomenon, such as surface energy decrease of C-S-H. Due to drying and heating, the internal surface energy is reduced, while creating a more stable structure and liberating certain amount of energy [19]. Higher release of energy allows microcracks to emerge. The change in contrast and brightness is noticed when relative humidity drops to 40%-50% RH, which is probably related to changes in free energy. This implies that changes of surface energy (Gibbs-Bangham shrinkage) should be related to changes in fracture energy, since some energy is liberated during drying.

When exposed to a cycles of wetting and drying (or vice versa), cracking appears scattered and may cover the entire stressed zone [20]. According to Goyal [21], the surface energy is dependent on moisture and the presence of moisture (after dry stadium) reduces the surface energy. Thus the crack in moist concrete (cement paste) may form or propagate quicker than in dry concrete, which can be compared with the cracking in presented cement paste samples 1 and 2.

More research on chemical and physical changes of microstructure during drying and moisture transport is needed for deeper understanding of the real cause of microcracking.
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REFERENCES


