PRELIMINARY INVESTIGATION OF DRYING SHRINKAGE CEMENT PASTE SPECIMENS

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Abstract

In order to perform drying shrinkage observations in ESEM (Environmental Scanning Electron Microscope), a preparation procedure for cement paste samples is developed. Instead of casting standard prisms (40 x 40 x 160 mm³), cement paste samples were cast in specially designed moulds of 30 x 30 x 2 mm³ and 10 x 10 x 2 mm³ in size. A special cylindrical tool was developed for polishing samples to the thickness of 1 mm or less. The sample observations as well as digital images of samples are acquired in ESEM. Images are analyzed to obtain displacements of the points of the cement paste samples due to the drying shrinkage.

Keywords: drying shrinkage, cement paste, mould, polishing tool, ESEM, digital images, drying shrinkage displacements.

1. Introduction

Microcracks appear in concrete structures before a mechanical load is applied due to moisture flow in the concrete microstructure. Moisture transfer is the highest in the interfacial transition zone (ITZ) between cement paste and aggregate. The main characteristic of the small (10-50 µm) ITZ is its higher porosity compared to a matrix and the existence of larger CH crystals. Higher porosity at micro scale affects the mechanical properties of concrete at the macro-scale. With a higher porosity, size and interconnectivity of pores is increased with a possibility of quicker drying or freezing, depending on w/c ratio, curing conditions and environment. As a consequence, the strength of the material is lowered. Due to the heterogeneous structure of concrete and differential expansion of concrete (due to thermal, freeze and thaw, sulfate attack and other related reasons) high tensile stresses may develop and subsequently microcracks. To improve durability of cement-based materials, research is focused on investigating the microstructure properties and micro cracking.

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is considered an ideal tool. Direct observations of the cement paste microstructure can be made creating environmental changes i.e. relative humidity (RH). Although the technology of electron microscope observations with SEM or ESEM is rather highly developed, the ITZ is extremely small and experimental observations are very challenging. A simulation of ITZ properties can be made by varying the w/c ratio and porosity in the cement paste samples, creating similar conditions as in the ITZ around different types of aggregate. Numerical simulations of drying shrinkage are considered as a helpful tool in addition to experiments. In order to perform computational analysis, drying shrinkage mechanism must be properly understood and the drying shrinkage deformations of the hydrated cement paste should be known.

2. Drying shrinkage: numerical solution

There are two ways to look at fluid flow in porous media: macroscopic (continuum approach where the movement of every point is described by the mathematical equation) and microscopic (when the molecular structure of the fluid is taken into account). Flow in porous media has the same principle as the flow in any vessel and it can be described with the governing differential equation (diffusion, D’Arcy’s law or Navier-Stokes equation). Complex phenomena such as moisture flow and drying shrinkage in porous media are very difficult to solve analytically [1] mainly because of the concrete randomness at any level [2]. The special boundary conditions [1] must be taken into account in order to specify the shape of the boundary in porous media geometry, the interaction between fluid and the walls, and other conditions.

Numerical solution is possible with a model of a complex 3-D network of voids, pores or capillaries of different sizes and shapes. This is a complex task. A simplified porous microstructure can be expressed as either a 1-D network of tubes of uniform diameter or a 2-D network (regular hexagonal, triangular, square or irregular lattice) [3].

In this research a Lattice Gas Automaton (LGA) was used as the numerical approximation of Navier-Stokes equation [4]. LGA is a discrete system of velocity, space and time, constructed as a fictitious micro-world with zero-dimensional particles, which propagate and collide on a regular triangular lattice. Numerical simulation of moisture flow in a sample subjected to drying shrinkage [5] was performed. The simulation of the moisture movement by means of LGA involves different collision rules among particles. This results in a different density (moisture content) at each node at every time step. The resulting moisture gradient calculations ($\Delta h$) are used to calculate drying shrinkage strain and stress, applying the following equations [6]:

$$\varepsilon_{sh} = \alpha_{sh} \Delta h$$  \hspace{1cm} (1)

$$\sigma_{sh} = \varepsilon_{sh} E$$  \hspace{1cm} (2)

where $\alpha_{sh}$ = drying shrinkage coefficient; $\varepsilon_{sh}$ = drying shrinkage strain; $E$ = Young’s modulus; $\sigma_{sh}$ = drying shrinkage stress.

3. Mechanisms of drying shrinkage

Complex drying shrinkage can be explained through different physical mechanisms: capillary tension, loss of interlayer water, changes in surface energy and disjoining pressure [7]. Different mechanisms operate at different levels of relative humidity. A distinction can also be made between real and apparent shrinkage mechanism [8]. Real shrinkage develops at the micro-scale and depends on the material structure properties. Apparent shrinkage appears at the macro-scale and depends on the geometry of the specimen. To be able to understand real rather than apparent shrinkage, very thin cement paste samples must be examined. In this way, the difference in shrinkage deformations between the interior and the surface is reduced.

Different types of experiments were performed on drying shrinkage leading to new findings. In the experiments in [9], drying shrinkage observations were made on cement paste prisms, making shrinkage measurements after the curing period under different conditions. It was shown...
that the relation of drying shrinkage and moisture loss depended on the curing conditions. The relation was linear only if the samples were not stored in water.

According to [10], drying shrinkage deformations and moisture loss (experiments on mortar) developed in time. The time-dependent moisture distribution in mortar was a linear function of the shrinkage deformation $\varepsilon_{sh}$ (Eq. 1) if the relative humidity (RH) remained above 45-50%. Recently [7], the experiments were performed on small cement paste samples. After curing in a saturated lime water and reaching a proper test age (4, 7 and 14 days), the drying shrinkage of the samples was observed in ESEM under different climate conditions (RH).

Many factors influence moisture flow and drying shrinkage. Some of the mentioned factors will be taken as variables in the research.
- Curing conditions (dry, moist, wet)
- W/C ratio – different water to cement ratio influences the permeability of the cement paste
- Cement types and cement particle size or specific surface area influence the hydration reaction rate. Throughout the entire reaction, the larger particles react more slowly.

4. Cement paste specimens

Unrestrained drying shrinkage experiments in the past were made with different sample shapes and sizes [7,9,10]. The usual procedure with prismatic samples is as follows. On one side of the prism, two metal markers are glued. After a curing period, the distance between the markers was measured (with a mechanical deformeter) as well as the sample weight and the unrestrained shrinkage was calculated. The prisms are made of cement paste, mortar or concrete. Observations of drying shrinkage take into account different w/c ratios and curing conditions for every specimen type. This method usually did not include any observations of the microstructure or gave any information about the microstructural changes. In order to do that, drying shrinkage should be observed on very thin (~1 mm) cement paste samples (flakes) [7].

Casting of prisms was also performed in the beginning of this research. Portland cement (type I, 32 R) and demineralized water were mixed (w/c = 0.45 and 0.5) in a Hobart mixer for 2 min. Cement paste was cast in standard moulds (40 x 40 x 160 mm$^3$), covered with a plastic cover and demoulded after two days. After curing under the different conditions in a period of 7 days, the prisms were sawn to smaller samples of 30 x 30 x 3 mm$^3$. The sample size was chosen such that it could fit in the ESEM XL30 stage.

In order to simulate 2-D drying shrinkage and to avoid steep moisture gradients in the vertical direction, the specimens should be very thin (to the order of µm). The usual procedure of thin sample preparation, where the thickness of the samples is expressed in microns could not be applied for unrestrained drying shrinkage. In that case, the sample is generally glued to a glass or plastic surface. This would obstruct drying shrinkage deformations. In order to assure free shrinkage, the specimen may not be glued to any substrate.

Although the sample is as 3-D object (it has a thickness of 1 mm) the shrinkage is considered as a 2-D problem assuming plane strain condition development.

It is almost impossible to cut a flat, 1 mm thick sample, since the cement paste is still very young (7 days old), and can not endure sawing without falling apart. The only way to avoid falling apart of the sample was to cut samples to the thickness of 2-3 mm which was still considered too large for our purpose. Generally, sawing of samples damaged the surface with scratches. In order to perform good microstructure observations in ESEM, sample surface preparation is critical for the successful imaging of the microstructure. The observed sample surface has to be polished flat in order to eliminate surface scratches, edge rounding, surface relief, and grain plucking and to reach thickness of 1 mm. Handling and polishing of a such young cement paste sample, is very difficult. It was necessary to find a right procedure, which will enable good sample preparation.
5. Moulds

In order to simplify the sample preparation and to avoid scratches from sawing and damaging of the sample in advance, stainless steel moulds were designed in two sizes 30 x 30 x 2 mm\(^3\) and 10 x 10 x 2 mm\(^3\) (Figs 1a, b). These moulds enabled demoulding after 2 to 3 days. Since we deal with the problem of drying shrinkage, it is considered desirable to demould samples earlier, even after 1 day. At that age cement paste samples are very soft and it is very difficult to demould samples without breaking them. The problem is solved with a thin plastic foil, which is placed at the bottom of the moulds. The foil prevents that the cement paste attacks to the mould.

6. Curing conditions

Demoulded samples are cured for 7 days under different relative humidity conditions as sealed (60%), moist (90%) and wet (100%). All samples are stored in the desiccators at 20\(^\circ\)C. Different RH (60% and 90%) were created by the addition of saturated solution of various salts: NaBr x 2H\(_2\)O and ZnSO\(_4\) x 7H\(_2\)O for 60% and 90% RH respectively. These solutions maintain the constant humidity inside the desiccators if the temperature stays constant at 20\(^\circ\)C. For the wet curing (RH = 100%), samples are immersed in lime-water at 20\(^\circ\)C. After the curing period, the samples are polished applying the cylindrical tool, specially designed for that purpose.

7. Cylinder for polishing (grinding)

In order to polish samples to the desired thickness, it was necessary to use a tool. The idea was to make a certain changes to an existing metal cylinder (Figs 2a, b, part 1) and to adapt it for handling the 1 mm thick samples. The solution was found in the implementation of a inner cylinder (Fig. 2a, part 2) (d = 30 mm and d = 10 mm) to the outer one, which should have edges on the outside (Figs 2a, b, part 3) such that the sample can fit in size. During polishing, a certain pressure on the top of the specimen is applied. For that purpose, the circular plate (Figs 2a, b, part 4) with a handle (Figs 2b, c, part 5) was made and screwed inside the outer cylinder (Fig. 2a, b, part 1). The handle from the plate is used as a marker of the desired sample thickness. A scale is made on the top of the cylinder (Fig. 2c, part 6). To measure the thickness of the samples in mm, the plate is screwed up and down such that the thickness can be controlled layer by layer. The specimen is placed on top of the plate (Fig. 2b, part 4).
8. ESEM observations and analysis of drying shrinkage

ESEM differs from the conventional SEM because it enables wet samples to be observed by eliminating air but allowing water vapour to fill up the chamber. Varying the pressure and the temperature within given limits, different ‘climates’ could be obtained creating different relative humidity conditions. For that purpose ESEM is usually supplied with a Peltier cooling stage. The size of the sample that can be placed in this stage is very small (less than 10 mm). A special stage was designed for cooling and heating of the chamber [11], which enabled the use of bigger sized samples (max 30 x 30 mm²).

The surface of the samples is observed with a GSE (gaseous secondary electron) detector, which enables sample observations in the wet mode. The GSE signal is translated to a digital image. Cooling and heating of the stage (Fig. 3, part 1) is provided by the plastic tube (Fig. 3 part 2). Cement paste samples (Fig. 3, part 3) are placed on the ESEM stage such that the bigger samples (30 x 30 x 1 mm³) cover the whole stage. For the smaller samples (10 x 10 x 1 mm³) a special PVC frame (Fig. 3, part 4) was made allowing unrestrained shrinkage. The temperature in the chamber is controlled from the top and the bottom of the samples with a specially designed thermocouple.

To simulate drying shrinkage, the RH is lowered from 99% to 20%. The pressure (5.3 torr) is kept constant while the...
temperature varies from 2.3°C to 26°C. Due to changes in RH and subsequent drying shrinkage the cement paste samples deform. If the sample would be covered by an imaginary square grid where every node in a grid has prescribed coordinates (x, y) it would be obvious that every node would be displaced during drying shrinkage [12]. Shrinkage is observed continuously as the sample dries out in ESEM. In Figure 4, an example of cement paste specimen at different RH (98.5% and 60%) is presented. Images of the same central point in ESEM (x = 0, y = 0) were taken at 500x magnification (the size bar in Fig. 4 is 50 μm). The drying shrinkage displacements are calculated using the VIC-2D program for correlating two (reference-undeformed vs. deformed digital) images. The displacement of every pixel in the chosen subset area is calculated in x-(u – displacement) and y-(v - displacement) direction. Figure 5 shows the range of movement of the center of every pixel in x and y direction. Since the sample was 28 days old, displacements were rather insignificant, with movements of up to 5 to 6 pixels only.

Manual measurements have been made in order to check the displacements of some randomly chosen points and to compare them to the results from the program (VIC-2D). Calculated displacements form the basis for the further determination of the drying shrinkage deformations and subsequently the shrinkage coefficient $\alpha_{sh}$.

Figure 4: Digital image of the cement paste sample (28 days old) under different drying conditions in ESEM, (a) RH = 98.5, (b) RH = 60%.

![Digital image of the cement paste sample](image1.png)

![Digital image of the cement paste sample](image2.png)

Figure 5: Results from the correlation analysis (VIC-2D program): displacement in (a) x-direction, (b) y-direction.

9. Conclusions

A cement paste sample preparation technique for obtaining digital images of drying shrinkage in cement paste has been presented. This technique includes a new way of sample preparation, which consists of sample casting in small stainless steel moulds and polishing by means of specially designed tool.

Sample preparation and optimally controlled curing conditions are extremely important for the proper observations of
cement paste microstructure and drying shrinkage in ESEM in the wet mode. The digital image analysis and deformation calculations present the basis for further research of cement microstructure as well as ITZ. Experiments are currently carried out and will be presented at the conference.

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