THE EFFECTS OF MOISTURE ON THE MICROSTRUCTURE
OF CEMENT-BASED MATERIALS

Progress Report

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ABSTRACT

The framework for a major reassessment of shrinkage in cement-based materials has been established. Two new techniques have been developed for this project and have been used to obtain significant new information. The techniques are: (1) specimen preparation and control of environment in an Environmental Scanning Electron Microscope in order to observe shrinkage and (2) a new image analysis technique called "Image Intensity Matching" which has been perfected and applied. It has become clear that progress in the area of shrinkage at the microstructural level can be accomplished by combining experimental observation with modeling. This approach employs image analysis to observe the small dimensional changes that occur upon drying and these results are used as constants in multi-scale modeling. In part this is true because the dimensional changes are small and require image analyses, and in part the combination is driven because the purpose of the research is to establish an ability to predict shrinkage.

An emerging goal of this research is to define the microstructure and the influence of moisture on microstructure in such a way that new predictive models can be developed. To this end recent results are:

- * Documentation of structure at early ages
- * Documentation of shrinkage at the particle level, ie the 1-10 micron level
- * Documentation of shrinkage at the particle cluster level, ie the 10-1000 micron level
- * Development of technique for investigating polished sections
- * Preliminary results of shrinkage at paste/aggregate interface

- * Documentation of shrinkage of paste as a function of water-cement ratio (w/c), composition, age of sample, curing temperature and relative humidity have been accomplished. C-S-H is the shrinking phase. **Pores have been found to expand during drying.**
- * A model which predicts the quantity of C-S-H and divides it into two types has been developed . This model predicts, for the first time, surface area as measured by H_2O , N_2 and larger molecules such as C_6H_{12} . The possibility that one of the two types of C-S-H shrinks more than the other has been suggested.
- * The foundation for a model that predicts shrinkage has been developed. This model divides the microstructure into different sizes, or scales, and, at each size, the appropriate mechanism is described mathematically. The different sizes are then chained together.

EXPERIMENTS

Recent research has focused on using a new image analysis technique developed for this project to explore the shrinkage behavior. The first result showed that only C-S-H shrinks. For portland cement an experimental matrix was chosen such that a few of the common variables are being investigated (see table 1). Shrinkage was measured using an image analysis technique developed during the early stages of the research. Both shrinkage of particles and shrinkage of groups of particles were measured. Shrinkage varied with changes in relative humidity, w/c, curing age, curing temperature, drying rate, and aggregate . Two magnifications, 1000x and 5000x, were used for each

sample. These magnifications correspond to looking at a small area and a single particle. Linear shrinkage is determined by taking the average of six measurements of change in the length across the area or particle. Shrinkage is relative to an initial condition and for this work all results are compared to imaging at 80% relative humidity as this was the first image taken.

The statistics obtained when making a few measurements of single particles or a small area in any sample are poor, thus experimental results presented are often the average of many results to overcome the inherent scatter of these measurements. Each experiment was performed twice to produce clear results but this alone was insufficient to provide accurate statistics. Similar averaging was used to look at the variation in shrinkage with other variables.

	w/c	age	curing temp.	other
SET I	0.3 0.4 0.5 0.6	7 days 14 days 28 days	20°C	
SET II	0.5	7 days 14 days 28 days	20°C 30°C 40°C	
SET III	0.5	7 days 14 days 28 days	20°C	slow drying normal drying fast drying

Table 1. Mix design for OPC pastes

Cement microstructure is composed of both shrinking and non-shrinking phases. Shrinkage therefore, is a composite behavior. The measured strain due to shrinkage for single particles is almost always greater than that of the measured shrinkage for area measurements. This is apparent in all of the Figs. 1-3 (pp. 5-7) and Figs. 4 & 5 (pp. 9-10). This difference can be accounted for because larger areas incorporate the effects of the restraints of non-shrinking phases. As shown later (Fig. 9), the modeling of shrinkage has shown that the restraining effect follows the volume fraction of non-shrinking phases.

Recent observations have demonstrated that pores expand on drying. Expansion occurs for measurements made across a region that contains a capillary pore. This is a new and important observation. These results are currently being organized for publication.

(a)

(b)

Figure 1. Shrinkage with age (w/c averaged) a. area b. particle

Age: The influence of age on shrinkage is shown in Fig. 1. As expected, younger specimens are associated with higher shrinkage.

Figure 2. Shrinkage with temperature (age data averaged) a. area b. particle

Temperature: The influence of temperature on shrinkage is shown in Fig. 2. Increased temperature is associated with reduced shrinkage.

(a)

(b)

Figure 3. Shrinkage with w/c (age data averaged) a. area b. particle

Water-cement ratio: The influence of w/c on shrinkage is shown in Fig. 3. Higher w/c is associated with increased shrinkage.

Drying Rate: The influence of drying rate on shrinkage is shown in Figs. 4 and 5. For the first time direct observation of microstructure shows that drying rate can have an influence on shrinkage. Fast drying results in less shrinkage.

Drying rate has long been anticipated to effect shrinkage, but often this effect is observed in large samples due to diffusion limited processes. A wide variation in shrinkage was measured for changes in drying rate for small samples, in which moisture diffusion limitations do not exist. A faster drying rate gave almost no shrinkage while a slow drying rate had a considerable shrinkage.

Influence of Aggregate: Preliminary results of shrinkage during the drying of mortars have been obtained in-situ in an environmental scanning electron microscope (ESEM). Deformations on the microstructural scale have been analyzed using recently developed computational techniques. Shrinkage depends strongly on the size and distribution of the aggregate at the microstructural level. Narrow spacing between aggregates and small aggregates lead to uniform shrinkage throughout the interface. Large aggregates and larger spacing between aggregates results in widely varying shrinkage in the interfacial zone. Also, displacement increases with distance from aggregate; in other words, since the strain is the slope of the displacement-distance curve, shrinkage is greatest next to the aggregate. For example see Fig. 6. This can be explained by the inhomogeneous distribution of the microstructural features. The presence of a pore leads to an expansion in the interfacial region.

(a)

(b)

Figure 4. Shrinkage with drying rate (age=7 days) a. area b. particle

Figure 5. Shrinkage with drying rate (age=28 days) a. area b. particle

Figure 6. Cement Paste Deformation in paste with two aggregates

Surface Area: BET surface area as measured by Nitrogen of all specimens is shown in Table 2 (below). A broad, but still preliminary, interpretation of this data is that specimens with smaller surface area exhibit smaller shrinkage.

Temperature Age	20° C	30° C	40° C
7 days	130.6	145.3	125.9
14 days	144.7	125.4	121.6
28 days	127.5	124.5	114.1

Table 2. Nitrogen surface area in m^2/g of C-S-H with changes in curing temperature

MODEL FOR C-S-H

A model has been developed that predicts quantitatively the volume of the major phases in hydrated cement pastes as a function of 1) the composition of the cement, 2) the degree of reaction, and 3) the initial water-cement ratio. This procedure is then used to develop a quantitative model for the surface area and volume of porosity that is accessible to nitrogen in C-S-H. An interpretation of the model is that there are two types of C-S-H, or perhaps regions within the C-S-H: one that nitrogen can penetrate and one that it cannot. Published values for surface areas and volume of pores are compared with the predictions made by the model.

MULTI-SCALE MODEL

The first step in multi-scale modelling is to separate the problem into several scales (see Figure 7 below), The four scale levels we have selected are the following: (1) a nanometer level because many currently accepted mechanisms for C-S-H shrinkage are at this level, (2) a micrometer level because it corresponds with the size of cement particles and thus the scale of the gross distribution of products, (3) a millimeter level because it encompasses the size of microcracks associated with moisture gradients, and (4) a meter level because short and long term shrinkage of structures are at this level.

Figure 7. Schematic of relationship between different scales of the multi-scale model

The advantage of multi-scale modelling is that many parameters that have appeared to be interlocked can be studied and formulated separately. Formulas and parameters obtained in the lower level model can be used directly as known quantities in an upper level model.

This model functions by using the finest scale model to generate input for the next coarser scale and this, in turn, provides input for a still coarser scale. In this way larger scale deformation is predicted based on fine scale mechanisms. This opens the door for a new generation of modelling. Specifically, models for the first time can be based on measured constants. A typical result is shown in Fig. 8.

Figure 8. Comparison of the model with test results

INFLUENCE OF RESTRAINT

As already discussed, the influence of restraint is significant. The multi-scale model can be used to make predictions of shrinkage in multiphase materials.

The framework of the model is a two-phase composites consisting of spherical non-shrinking particles embedded in a continuous shrinking phase. In C_3S paste, the shrinking phase consists of C-S-H and porosity, while the non-shrinking particles are CH and anhydrous cores. The effect of constraint by the non-shrinking particles on the composite shrinkage is given by Equation 1.

$$\frac{\epsilon_{composite}}{\epsilon_{shrinking}} = 1 - \frac{c_{non-shrinking} \left(\frac{K_{non-shrinking}}{K_{shrinking}} \right)}{1 + \left(\frac{K_{non-shrinking}}{K_{shrinking}} - 1 \right) \left(\frac{3 + 4c_{non-shrinking} \frac{G_{shrinking}}{K_{shrinking}}}{3 + 4 \frac{G_{shrinking}}{K_{shrinking}}} \right)}$$

Equation 1.

This formulation is shown in graphical form in Figure 9. For materials having the same modulus, the composite shrinkage decreases linearly with the volume of the non-shrinking phase. If the ratio of moduli is much greater than 1, the composite shrinkage will be reduced further.

Figure 9. Composite shrinkage from multi-scale model

SUMMARY

Shrinkage in cement-based materials involves a variety of mechanisms operating over a broad range of scales, from the nanometer level to the meter level. Because bulk shrinkage is the result of combining deformations at several scale levels, multi-scale experiments and mathematical models are important and necessary.

Experimental procedures at micrometer level, ESEM and our new image analysis technique, Image Intensity Mapping Technique (IIMT), have been developed and used for studying the shrinkage of cement paste. The new results at micrometer level show:

- (1) Hydration products of C_3S and C_2S exhibit large shrinkage at the micron level, and those of C_3A and C_4AF appear to move as clusters and do not show shrinkage at the micron level;
- (2) Interparticle shrinkage is larger than intraparticle shrinkage, which suggests that the material linking individual grains has a higher water content than the interior of the grains;
- (3) The unrestrained shrinkage tests of cement paste indicate that the trends in the dependencies on water-to-cement ratio and relative humidity are the same as those in large scale tests, but the values are much higher at the smaller micrometer level. However, the fine scale shrinkage is independent of age (degree of hydration), and this behavior is completely different from that of large scale tests;
- (4) Shrinkage in the interfacial zone depends on the size of aggregates and the distance between aggregates; large aggregates and large spacing between aggregates results in non-uniform shrinkage in the matrix;
- (5) Capillary pores exhibit large changes in shape on drying, which can not be explained by a simple composite model

Based on the test results at nanometer and micrometer levels, theoretical models are being developed. These include: (1) A model for the structure of C-S-H at the nanometer level which quantitatively evaluates surface area and volume of various solids and pores. Based on this model, the dried density, saturated density and equivalent spherical diameter of a basic C-S-H particle can be predicted; (2) A multi-scale model of shrinkage.

HIGHLIGHTS

A great deal of new information about shrinkage at the microstructural level has been acquired. Experiments and computer analysis serve as a basis for modelling.

Some highlights of our results are:

- * C-S-H shrinks and values for dimensional change are being determined.
- * There may be two types of C-S-H, only one of which shrinks.
- * All other phases serve as restraints to shrinkage.
- * Pores expand on drying and therefore may be a mechanism for the "size effect", in addition to microcracks.

PUBLICATIONS

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