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

Progress Report

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Abstract

New experimental techniques that allow the precise measurement of drying shrinkage of cement-based materials within the Environmental Scanning Electron Microscope have been developed. Accuracies of approximately 1% can be obtained on images as small as 20x20 pixels. Preliminary results on the shrinking of these materials has been obtained and quantitatively analyzed to produce "maps" of the deformation process. Samples have been dried from saturation in environments which are approximately 25% relative humidity, and deformation has been evaluated for the model materials C3S, C3A, and C4AF. The bulk of the effort during this initial period has been to establish the sophisticated experimental techniques which are necessary to pursue the proposed research. In this respect, the initial stage has been extremely successful and we have begun the process of detailed, methodical, documentation of the deformation of both the model materials and ordinary portland cement paste. The possibility of measuring the constraining effects of other phases such as aggregate is now being investigated. These initial results have resulted in four publications. Two publications are of a review nature and two are the reporting our new experimental technique, and initial results. The latter two are being submitted to peer reviewed journals.

Background

This is a progress report for the first 12 months of the research program aimed at establishing a microstructural explanation for shrinkage due to drying in cement-based materials. A number of separate efforts have been pursued. The first important task has been the identification and hiring of a post-doc and

a graduate student. Both of these individuals have started and made significant progress in spite of the fact that this is a new project and one which very much is relying on brand new experimental technology. Specifically, the Environmental Scanning Electron Microscope (ESEM) is the major instrument employed in this research and it has been shown that new experimental techniques are required along with very sensitive image analysis. We have started collecting and analyzing relevant data and some of our initial observations have already proven to be significant. This report will discuss several of the accomplishments which have so far been obtained.

As a basis for defining the research that is necessary for this program, an extensive literature search has been undertaken and review article has been written (1). The objective of the article is to review the mathematical formulations for shrinkage in such a way that the microstructural observations that we are making can be made relevant to models already in place. Where models are not complete, we will formulate our results so that they can be used as the basis for future modeling.

Experimental Technique for Observing Shrinkage in the Environmental Scanning Electron Microscope

During the early stages of our research, we discovered that, except for the extreme cases of shrinkage, most of the microstructural changes that were taking place could not be observed by simply comparing two images (by the naked eye), one before and one after drying. Even attempts to overlay the image proved to be unsuccessful. Certainly no quantitative information could be obtained. We

have developed a new sophisticated quantitative technique. There are two components: 1) microscopic and 2) image analysis.

The basic microscopic experiment involves looking at cement paste, at a given age and equilibrating the sample with a specific relative humidity, and preparing micrographs at each stage. We have generated dozens of micrographs of different representative cement-based materials.

A major development activity was undertaken in order to compare two micrographs pixel by pixel and thus determine quantitatively any movement in the microstructure. Elongation, rotation and shear are measured using a new sophisticated analytical package. A digital image correlation analyses has been developed to compare the location, and therefore deformation, of individual points within a microstructure. This technique is summarized in figure 1. Two images, initial and deformed, are taken with the ESEM at a magnification suitable for isolation of individual microstructural features (approximately 5000x to give features of size near $1\mu\text{m}$). These images are stored as digital arrays (512x512) which allow them to be mathematically manipulated. A small window (20x20 pixels) is chosen from the original image and a larger search window (50x50 pixels) is chosen from the deformed image. Because the conditions of the two images, contrast and brightness, may vary, these windows are normalized to identical distributions. Two surfaces are created from the digital information and a subsequent computer intensive numerical solution gives displacements that minimize the error between the surfaces. Output from the analyses includes displacement, expansion (or shrinkage), and shear.

It is important to realize that the results from the correlation analysis are an arbitrary displacement field and must be referenced. For simplicity, the center point in the initial image is matched to the corresponding point in the deformed image and this deformation is then subtracted from all points to give a point of reference. Thus, the center of the image is "pinned."

The deformations of importance for cement systems are 1% or less. For the digital images with 512x512 pixels, this suggests a minimum resolution of 5 pixels is needed over the entire image. However, this would require analysis of the entire image without isolation of individual features. This raises the question of the resolution of the image correlation analysis. For example, the resolution required to determine a 1% shrinkage in a 20x20 pixel feature is 0.2 pixels. This subpixel resolution is possible since the correlation analysis interpolates and creates a surface from the original pixel data, and thus matches two surfaces and not just two arrays of numbers.

The resolution of the correlation analyses may be as small as 0.1 pixel. This has been verified for cement images using the following technique. An original image of larger size, 1024x1024, was taken. From this image a smaller image was created by averaging an area within the larger image. For example, a 512x512 image was created by averaging every 4 pixels in the original image. Shifting the original image 1 pixel and repeating the averaging resulted in simulating a shift of .5 pixel. This was repeated to shifts as low as .0625 of a pixel.

The results from the correlation analyses of these simulated shifts are shown below.

Simulated Shift	Calculated Shift	Standard Deviation
1.0	1.0	-
0.5	0.501	-
0.25	0.237	0.014
0.125	0.106	0.062
0.0625	results not reliable	results not reliable

These results show simply that the correlation analysis is capable of subpixel shift determination. However, as the shifts become extremely small the results are overshadowed by large deviations. Thus, the practical limit of the correlation analysis is approximately 0.2 pixels. This level would be sufficient to determine a 1% deformation in a 20 pixel feature. The feasibility of accurately measuring shrinkage of cement-based materials in the ESEM has been demonstrated.

Initial Experimental Results

Three model cement systems have been used initially to isolate shrinkage behavior to individual hydration products. These systems are C3S, C4AF, and C3A. Each system was mixed with twice the water necessary to satisfy simple stoichiometry of the product. For example, it was assumed that C3S mixed with water formed C3S2H3. Errors in these ratios are well known but hydration would proceed unhindered with excess water.

A test of weight loss within the ESEM chamber was conducted to get an idea of the amount of water that is lost during a given time. There are many possible variables for a test such as this, but for simplicity room temperature and a pressure of 5 torr was chosen. Thus, the weight loss was observed only as a function of time. These measurements were made on thin section of C3S hydrate and a small scoop (hydrate is not binding) of C4AF and C3A hydrate. Results are shown in figure 2.

The weight loss for each hydrate followed a similar path. An initial rapid loss that would be excess water followed by continued removal of other water. the important feature is that all the water that will be removed at 5 torr is complete after approximately 30 minutes. Thus the dynamic observation of shrinkage for these sample images must be taken at a time well before 30 minutes. If images were exclusively taken at 30 minutes and 60 minutes for these experiments. This should then show some shrinkage between the first two images and no shrinkage between the second two images.

The shrinkage results for the three systems are shown in figures 3,4 and 5. These figures show the results between 10 minutes and 30 minutes. All shifts are shown by arrows which are a magnification of the actual shifts (notice the points are very close since the shifts involved are small) and are referenced to the point closet the center of the image.

The shrinkage of C3S hydration products appears relatively uniform with almost all points moving toward the center. This is expected for a shrinking body. There is a necessity to define the actual magnitude of the shrinkage in this type

of diagram. Since we are measuring individual point the shrinkage can be calculated from any two points. To get accurate values, the two points chosen must be on opposite sides of the reference point. After doing this, the shrinkage for these individual hydration clusters was found to be approximately 1%. This has been termed interparticle shrinkage.

Analysis of intraparticle shrinkage is shown in figure 6. Here the shrinkage for a single particle is exclusively inward and again relatively uniform. The magnitude for this shrinkage is again approximately 1%.

The C3A and C4AF hydration product results are quite different. These both do not show any uniformity across the entire image but do show local uniformity. This is the result of the products shifting as clusters. Some areas move drastically and other areas are stationary.

It must be noted that no shrinkage was observed between the 30 and 60 minute images for all three samples and is therefore not shown.

Overall, these results show great promise, we are able to document insitu deformation for the first time on a scale comparable to the features of cement hydration products.

Future Research

With these preliminary results completed the focus during the next months will broaden and tie up some loose ends.

The examples cited above for a single pressure and after 10 minutes. Attention will be paid to the initial water loss when perhaps the greatest shrinkage may occur. Thus, the shrinkage from 100% relative humidity must be documented. The ESEM chamber allows complete control of humidity and thus we should be able to rewet and redry a sample to check for reversible and irreversible effects.

It is necessary to measure shrinkage of larger samples within the ESEM under equivalent condition to determine any size effect. This is very critical in the determination of the constraint and cracking that occurs in large samples and is not observed at the microstructural level.

The preliminary results were on model systems but the focus will shift to OPC to determine the interplay between phases as shrinkage occurs. Finally, the influence of restraining effects on aggregate will be investigated.

Image Correlation Technique

Fig.1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Bibliography

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