Modelling drying shrinkage of cement paste and mortar
Part 1. Structural models from nanometres to millimetres

DALE P. BENTZ¹, DANIEL A. QUENARD², VERONIQUE BAROGHEL-BOUNY³, EDWARD J. GARBOCZI¹, HAMLIN M. JENNINGS⁴

¹ Building Materials Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
² Centre Scientifique et Technique du Bâtiment, 38400 Saint-Martin d'Hères, France
³ Laboratoire Central des Ponts et Chaussées, 75732 Paris, France
⁴ Departments of Civil Engineering and Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

The nanostructure of calcium silicate hydrate (C-S-H) gel contributes to many physical properties of concrete, including the important engineering properties of creep and shrinkage. A set of structural models for this gel and computational techniques for their validation have been developed. The basic nanostructure of C-S-H is conceived as a self-similar agglomeration of spherical particles at two levels (diameters of 5 nm and 40 nm). Computational techniques are presented for simulating transmission electron microscopy images and computing sorption characteristics of the model nanostructures. Agreement with available experimental data is reasonable. The development of these nanostructural models is a first step in a multi-scale approach to computing the drying shrinkage of model cement-based materials. Such an approach will provide a better understanding of the relationships between microstructure and the shrinkage behaviour of these systems.

1. INTRODUCTION

While the drying shrinkage of concrete has been studied extensively, it is only recently that the need to relate microstructure to basic mechanisms has been emphasized [1–3]. From the authors' perspective, this step is seen as a necessity to aid in the validation of proposed mechanisms [4, 5] and for the development of material parameter based models to predict the shrinkage behaviour of structures. A major obstacle in elucidating these relationships is the wide range of scales existing between the observed shrinkage behaviour of 1 m³ samples of concrete and the controlling physical processes (capillary condensation, etc.) occurring at or below the nanometre level in the 'gel' phase of the cement paste. For many of the size levels in between these two extremes, the material exhibits a heterogeneous structure which may need to be accounted for either explicitly or statistically in models of shrinkage behaviour. Examples of this heterogeneity include: the cement paste microstructure at the micrometre level which consists of unhydrated cement particles, gel, crystalline hydration products such as calcium hydroxide, and porosity, and the concrete itself at the scale of millimetres, consisting of cement paste, aggregates, and air voids.

Currently, computational capabilities do not exist which would allow one to consider directly the heterogeneity present at these different scales in a single model. Thus, the use of a multi-scale approach [2, 6] is necessitated. Here, a number of structural models are developed, each at a different scale. The property information computed at one scale is used as input into the next higher scale. For example, properties computed from a model of the nanostructure of the calcium silicate hydrate (C-S-H) gel can be used as input for the gel phase of a micrometre level cement paste model. Likewise, the properties computed here can be input into a millimetre level model of mortar or concrete. Because a complete set of models has not yet been developed and validated, an unanswered question remains as to the extent to which properties computed for a phase at one level can be homogenized at a higher level. For example, can the properties of the C-S-H gel be considered homogeneous at the micrometre level or are there differences between the inner and outer products that must be taken into account [2]? One example where inhomogeneity must be considered explicitly is the cement paste near an aggregate (the interfacial zone) in conventional concrete, which has a different microstructure and properties from the bulk cement paste [6]. Here, the paste heterogeneity can be accounted for explicitly in performance models [7], as the concrete must be considered as a three-phase material [8], even when air voids are ignored.

At each scale of interest, different analytical techniques for probing the structure of a material are available. At the micrometre level, pore structure can be measured indirectly using mercury intrusion porosimetry and the microstructure can be directly observed also using scanning electron microscopy (SEM) [9] or x-ray microtomography [10]. At the nanometre level, the structure of the C-S-H gel can be inferred from sorption experiments [11]. At this level, small angle neutron scattering (SANS) is a useful nondestructive evaluation technique, providing a scattering profile representing a
Fourier transform of the sample nanostructure [12, 13] which can be analyzed to obtain pore surface area directly. Still, structural interpretations of these measurements can be confirmed only partially by high resolution transmission electron microscopy (TEM) [14], with a resolution limit of the order of tens of nanometres, whereas the actual structure exists at levels of nanometres and tenths of nanometres. Atomic force microscopy (AFM) may offer one means of observing the gel structure directly at the nanometre level.

Our goal in the present work is to develop a set of computational tools which allows the generation of structures at a variety of scales and the subsequent calculation of properties and production of computer images in order to validate the structural models against experimental measurements. Because structural models of cement paste at the micrometre level have been developed previously [2, 6, 15], in this paper, we concentrate on the nanometre level structure of the C-S-H gel, with the ultimate goal of linking to the existing models for cement paste. We will consider agglomeration of nanometre scale spherical particles as the basic model for the structure of C-S-H at this level. Although not considered here, one might also be interested in the 'crystalline' or layer structure of the C-S-H within each spherical particle. While no definitely proven structure has been determined at this level, it should be noted that progress is being made towards accurately identifying this crystalline structure [16, 17], which could be important for understanding certain aspects of drying shrinkage, such as the irreversible shrinkage observed during a first drying [18]. Once a reasonable set of structural models has been developed, one can proceed to investigate shrinkage mechanisms using finite element techniques [19].

2. COMPUTATIONAL TECHNIQUES

2.1 Nanostructure

The basic model for the structure of C-S-H at the nanometre level is based on a hard core–soft shell representation [20]. The individual C-S-H particles are represented as spheres, each consisting of an impenetrable hard core surrounded by a concentric soft shell which can overlap freely both the hard cores and the soft shells of other particles. While any size distribution of particles can be matched using the model [21], for simplicity, we will limit our representations to monosize particles. The particles will be placed in a three-dimensional cubic box using periodic boundary conditions such that a desired interparticle porosity is achieved. For C-S-H, some overlap of these ideal spherical particles is necessary to achieve the desired low porosities (lower than dense sphere packings), as is also indicated in observing TEM images of the gel [14].

This continuum representation can then be digitized at various resolutions for the production of images and computation of properties as described below. For example, a 3-D system of side 25 nm can be digitized into a 3D array of $200^3$ pixels where each pixel is of side 0.125 nm. For this model, the size of the individual spheres must be chosen; here, it will be based on an existing interpretation of SANS data from the literature [12], as detailed in the results section.

For our model C-S-H structure, a two-level (macro/micro) 'self-similar' structure will be generated to represent the C-S-H particles between scales of 1 nm and 100 nm. The C-S-H will be considered as a system of 'large' (tens of nanometres) spherical agglomerates, each composed of many smaller (nanometre size) spherical particles. Such a self-similar multi-scale model is not uncommon for gel-like materials, as it serves as a conceptual basis for structural models of aerogels [22]. Evidence for such a structure for C-S-H is provided by SANS data and TEM images [12–14].

2.2 Image production

For comparison against images of real structures, it is quite useful to be able to produce simulated TEM and other types of images of structures existing only within the computer. To simulate a TEM image, one selects a given thickness section of the three-dimensional continuum structure, digitizes it into a 3D image (cubic array, $J(x, y, z)$, typically 256 on a side), and simply sets the intensity of each pixel in the simulated TEM image according to

$$I(x, y) = f(x) \times \sum_{z} (1 - J(x, y, z))$$

where $J(x, y, z)$ is equal to 1 for pixels digitized as solids and 0 for pixels digitized as porosity and $f(x)$ is an arbitrary weighting function taken as equal to one in the examples provided in this paper. To compare against real TEM images, it is of interest to superimpose the sub-nanometre level texture of the gel onto an image generated at the macro level. This can be achieved approximately by generating a TEM at the tenths of a nanometre scale, rescaling it to match the scale of the macro image, and using a maximum operation (at each pixel, the resultant image is composed of the maximum grey level present in the two component images) to combine the two images.

One can also simulate atomic force microscopy images using these same principles. Here, after the 3D digitization, the 2D image intensities are computed as

$$I(x, y) = C - \min_{z} \{z: J(x, y, z) = 1\}$$

where $\min_{z} \{z: J(x, y, z) = 1\}$ indicates the depth in the sample at which solid material is first encountered and the value is subtracted from C (e.g., 255 for an 8-bit grey level representation) to obtain the desired effect that solids closer to the surface in contact with the AFM tip ($z = 0$) are brighter. Fig. 1 shows a simulated AFM image for the micro-level structure of the model C-S-H. The ability to produce such images allows a direct comparison.