Chemical Aging and the Colloidal Structure of the C-S-H Gel: Implications for Creep and Shrinkage

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Implications for a colloid model for C-S-H on creep and shrinkage are discussed. A basic thesis of this paper is that C-S-H undergoes chemical aging, causing it to become stiffer, stronger, and denser over time. This process is accelerated by increased temperature and also by drying, which introduces large local strains that may provide a microstructural basis for creep sites. This chemical aging process of C-S-H can thus affect many of the physical properties of cement paste, and there is particular relevance for the complex shrinkage and creep behavior of this material. A broader definition of aging is used in certain mathematical models of creep and therefore new definitions should be considered. It is hoped that separating chemical aging effects from other changes, such as continued hydration, may lead to a better understanding of the microstructural causes of creep and shrinkage.

1. INTRODUCTION

Recognition of the colloidal and gel-like properties of cement paste, and of the C-S-H component in particular, dates back to the 1950s with the work of Powers and his colleagues at the Portland Cement Association [e.g. 1]. However, during the intervening half century of research the colloidal properties of the C-S-H gel were often downplayed in favor of structural interpretations based on naturally-occurring minerals such as tobermorite and jennite. Because these minerals have a layered structure, the existence of "interlayer spaces" in the C-S-H gel containing strongly adsorbed water was postulated and has been incorporated into most C-S-H models, including the well known Feldman-Sereda model [2]. These models have been fairly successful at qualitatively explaining the shrinkage behavior and gas sorption properties of cement paste. However, emphasis on the layered structure of C-S-H has meant that the colloidal properties have not been fully developed. The so-called Munich model [3] is based on some of the concepts of colloidal science, relying particularly on the idea of a disjoining pressure between particles. However, this model does not address changes that occur in the saturated state.

Considering the C-S-H in cement paste to be structurally a colloidal gel has implications for both creep and shrinkage, particularly when combined with the phenomenon of chemical aging. In this context, a careful definition of aging is required to avoid confusion.

*Cement chemistry notation: C=CaO, S=SiO$_2$, H=H$_2$O
To agree with conventions of sol-gel science, the term aging in cement should include only those changes that occur independently of the hydration reactions. It is well established that the properties of cement paste stored under saturated conditions at room temperature continue to change long after the hydration reaction has stopped. These changes include increases in the specific surface area measured by gas sorption and changes to the pore size distribution.

The complex creep and shrinkage behavior of concrete has been the subject of intensive investigation, both experimentally and by mathematical modeling. A major complication is introduced by the fact that the microstructure of cement paste continues to change at the same time that it undergoes loading and/or drying. In this context the term aging generally includes changes due to both increased hydration of the cement particles and changes in the microstructure of the products after they form.

A number of theories attempt to explain the complicated effects of aging on creep and shrinkage. Perhaps the most sophisticated mathematical theory of creep relies on the concept of microprestresses [4], which are attributed to volume changes as hydration product forms as well as changes in disjoining pressure. The presence of these "creep sites" increases the ease of bond breakage, increasing the creep rate. With this theory, freshly produced hydration product contains a relatively high density of these sites, but over time the stresses relax, reducing the susceptibility to creep. Environmental changes such as drying and rewetting and heating and cooling have the effect of increasing the density of creep sites. However, there are fundamental chemical and thermodynamic arguments against the idea of forming C-S-H in the saturated state with high internal stresses that could act as creep sites.

Recently, a new model for the structure of the C-S-H gel has been proposed [5], based on aggregations of roughly equiaxed colloidal-scale C-S-H particles with no layered structure on a scale greater than a few nanometers. This model rationalizes a variety of observations and measurements, allowing specific surface area, density, and composition to be predicted as a function of relative humidity. Although this model has not been fully developed in terms of predicting properties such as creep and shrinkage, it can be interpreted with sufficient detail to provide some new meaning to the concept of creep sites. First, however, it is worth reviewing some basic concepts in colloid science.

2. INORGANIC SOL GEL PROCESSING

The term "sol gel" refers to the preparation of ceramic materials by causing a solution of fine colloidal particles (the sol) to link together into a continuous solid phase (the gel). The solvent is then removed from the gel, leaving a highly porous solid that may be fired to increase its strength or to sinter it into a dense body. Applications of sol gel processing include porous membranes, sensors, insulation, optical and protective films, and bulk optical glass. Although sol-gel processing has been around since at least the 1930s, there has been a significant increase in interest in this field since the early 1980s, as evidenced by the number of scientific papers published and patents granted [6].

The growth of the sol-gel processing field has naturally led to an increased understanding of the fundamental properties of inorganic gels, and there is now a wealth of scientific and technical literature, which was not available to earlier cements researchers. The valuable book by Brinker and Scherer [6] summarizes and distills a huge amount of information on sol gel processing and the properties of gels.
The key reaction in a sol gel process is the linking of hydrolyzed molecules together, called condensation. In its simplest form, condensation can be written as

\[-\text{Si-OH} + \text{HO-Si-} \rightarrow \text{-Si-O-Si-} + \text{H}_2\text{O}\]  

This reaction, which liberates a water molecule, is the fundamental mechanism for linking monomeric species into polymeric clusters that grow and evolve into particles or gels. The morphology of the solid product (gel) depends strongly on the degree of reversibility of the condensation reaction. A porous, space-filling gel will form only when the condensation reaction is nearly irreversible, i.e. clusters "hit and stick". In this case, the clusters grow into diffuse fractal structures that occupy more and more of the sol, eventually linking together into a continuous gel.

If the rate of bond-forming reaction (condensation) is only slightly higher than that of the reverse (bond breaking) reaction, then a very different situation develops. As the polymeric clusters grow by adding new monomers, they also restructure and reorganize themselves, creating more and more crosslinks and becoming increasingly dense. Eventually solid, dense particles are formed that fill only a small fraction of the original sol volume.

Under conditions intermediate between these cases, highly cross-linked clusters grow in size until they are large enough to settle out of the suspension. These colloidal precipitates are gel-like, in that their internal structure contains colloidal-sized regions of liquid and solid, but they are too dense to fill the entire space and so the overall system does not become a true gel. According to Scherer [7], the C-S-H phase of cements is a colloidal precipitate of this nature. The presence of capillary porosity in cement pastes is good evidence of this, as it represents the volume fraction of sol that was not filled by the precipitated clusters.

It should be noted that precipitation from solution does not produce gels with high internal stresses unless the gel is dried. In general, even precipitation of larger crystalline phases does not produce large stresses unless the free energy change driving the reaction is very large, which is not the case for C-S-H forming from the aqueous phase.

3. AGING OF INORGANIC GELS

Aging of a gel is defined as changes in the structure and properties that occur under ambient or hydrothermal conditions. For inorganic gels formed by a sol gel process, the condensation reactions that drive the sol-gel transition (eq. 1) can continue long after gelation, causing a continued increase in the polymerization of the silicate network. This is the root cause of the multiple effects known collectively as aging. The most significant result of aging is generally an increase in the strength and stiffness of the gel. Condensation reactions, and thus aging, are accelerated at higher temperatures. In a highly porous (space-filling) gel, continued condensation reactions bind together the flexible branches of the silicate network. This phenomenon, known as syneresis, causes the solid phase to shrink uniformly and expel the pore fluid. The gel volume can decrease significantly, while maintaining its shape.

4. EFFECTS OF AGING ON CEMENT PASTE

The degree of polymerization of the silicates in cement paste has been measured by both the trimethylsilylation technique and by NMR. Results have shown that there is a progressive polymerization of the silicate with hydration time, and that this process is greatly accelerated by temperature [8]. It is thus established that cement paste undergoes chemical
aging, and this is completely consistent with the hypothesis that C-S-H is a colloid. Due to the activation energy for condensation of the silicates, aging processes in cement are particularly apparent when comparing pastes with different hydration temperature histories.

Because cement paste contains significant amounts of non-gel phases, i.e. restraining phases, it is difficult for the solid network as a whole to contract spontaneously and syneresis is not commonly observed. However, small amounts of syneresis can be observed during the first few hours of cement hydration when the paste is plastic [9]. After set, macroscopic shrinkage of the paste via syneresis does not occur.

When cement is hydrated at elevated temperatures the precipitated C-S-H undergoes an increased rate of silicate condensation, causing the bound water content to be lower and the density to be higher. Consequently, the capillary porosity is higher than it is at lower temperatures, and this increases the macroscopic permeability and reduces the strength of the cement. Interestingly, heating a hardened cement paste even for a short period of time after hydrating at normal temperatures increases the amount of silicate polymerization and causes many of the macroscopic effects associated with continuous high temperature curing [10,11].

Applying a short heat treatment to cement paste is a valuable way to study the effects of aging because differences in degree of hydration caused by a higher hydration temperature can be minimized. After a short heat treatment at 60°C, the surface area of hardened cement paste as measured by nitrogen gas sorption is increased by up to 50% [12]. However, when the surface area is measured by small-angle neutron scattering (SANS) the surface area is virtually unchanged [13]. Since gas sorption requires drying pretreatment while SANS is conducted on a saturated sample. We hypothesize that the heat treatment polymerizes and stiffens the C-S-H phase, causing it to collapse less on drying and allowing more of the internal porosity to be accessed by nitrogen. This effect is closely related to the effects of aging on drying shrinkage, discussed next.

### 4.1 Drying Shrinkage

Drying shrinkage in cement paste can be divided into reversible and irreversible components. Irreversible shrinkage is the final change in length after the specimen has been dried and resaturated. The primary driving force for shrinkage at relative humidity (RH) levels from 100% down to around 50% is capillary tension in the pores, and disjoining pressure between the particles of cement. Both of these processes are intrinsically reversible, so irreversible shrinkage strains must result from physical or chemical changes to the paste.

Aging of cement paste reduces the total amount of shrinkage on drying, in that older pastes and pastes hydrated at elevated temperatures shrink less on drying to a given RH. As was first noted by Parrott [10], application of a short heat treatment at 60°C to cement paste also reduces subsequent drying shrinkage. In fact, it is primarily the irreversible component of shrinkage that is reduced by aging; heat treatment at 65°C can reduce irreversible shrinkage by two thirds [14]. In other words C-S-H does not undergo as much collapse or rearrangement after it ages.

There are a few different mechanisms by which aging of a gel can affect drying shrinkage. First, the polymerization reactions that constitute aging (eq. 1) increase the stiffness (modulus) of the gel. Thus, when a given compressive stress is applied to the gel, the shrinkage strain is lower after aging. Another effect of aging is to change the pore size distribution of the gel. For cement paste, this is most easily observed by comparing pore
volumes of pastes hydrated at different temperatures. Bentur [15] found that a C₃S paste hydrated at 65°C had more capillary porosity but less mesoporosity than a similar paste hydrated at 25°C. In agreement with these results, Parrott [11] found that the weight loss on drying to 85% RH was increased by a short 60°C heat treatment, while the weight loss between 85% and 55% RH was decreased. Drying to equilibrium at a given RH empties all pores larger than a given size determined from the Kelvin equation. The shrinkage stress applied to the paste depends on both the size of the smallest pores emptied and on the volume fraction of these pores. Thus, by decreasing the mesoporosity responsible for drying stresses at moderate RH levels, aging can reduce the driving force for shrinkage.

The above mechanisms provide explanations for lower total shrinkage and reversible shrinkage as a result of aging, but would not affect irreversible shrinkage. As noted above, irreversible shrinkage is puzzling from a purely physical point of view because all of the mechanisms of drying shrinkage are intrinsically reversible. The known behavior of pure inorganic gels can provide an answer [6]. As a highly porous gel dries and shrinks, adjacent areas of the silicate network come into closer contact, giving them the opportunity to bond together via condensation. This reaction is not reversible, so on resaturation (when the stresses are relaxed) the gel does not return to its original dimensions. This process is similar to syneresis, but the process is driven by the compression of the gel during drying. The colloid model [5] suggests that irreversible shrinkage is due to rearrangement of the C-S-H particles into a denser packing arrangement, as well as increased bonding between particles.

Postulating a mechanism of this type for cement paste allows many aspects of irreversible shrinkage to be explained. When a paste already has a high degree of silicate polymerization prior drying then little if any further bonding can occur during drying, so aged pastes undergo little irreversible shrinkage. On the other hand, because this mechanism densifies the gel it explains why young (unaged) pastes exhibit not only significant irreversible shrinkage but also increased capillary porosity and permeability after drying. Such a mechanism also provides a ready explanation for the observation that pastes that are dried and resaturated twice develop much less irreversible shrinkage during the second cycle.

There is direct evidence for this mechanism as well: the degree of polymerization of the silicate in young cement pastes has been observed to increase significantly after drying and rewetting [16]. One is left with the interesting conclusion that the drying process itself causes aging of cement paste.

4.2 Drying and Creep Sites

The structure and properties of gels are strongly influenced by changes in temperature and relative humidity. For example, gels can shrink by huge amounts upon drying, and moisture gradients or the presence of restraining phases can generate high local stresses. If C-S-H is subjected to drying it also can easily experience the conditions that could produce the microprestress sites proposed by Bazant [4]. This is particularly true if C-S-H is mixed with fine material that acts as restraints to deformation as are the case in cement paste. In other words the stresses that cause a gel to collapse during drying, are sufficient to cause local fracture within the gel and they certainly could leave residual stresses that would facilitate creep when an external load is applied.

In order to investigate this type of deformation at the micron level a technique has been developed that compares two digital images, one before and one after deformation. The technique is called Deformation Mapping Technique (DMT), and it has been used to measure
local deformations as cement paste dries [17]. The DMT has shown that as a paste dries the microstructure experiences large local regions of compaction and rarefaction, and that the abundance and magnitude of the deformations depends on variables like age and initial w/c of the paste. These deformations represent a type of feature in the microstructure that may be related directly to properties such as creep and shrinkage. Furthermore the highly strained rarefactions could easily act as sites where bonds break more easily than they would in the pre-dried saturated state. If this is so then they represent a microstructural feature that can be quantitatively measured and used as input to mathematical models.

5. SUMMARY

From the point of view of modeling creep and shrinkage, aging is the result of three phenomena: 1) increases in degree of hydration 2) the precipitation and polymerization of C-S-H and 3) internal local stresses introduced by changes in relative humidity and temperature. The first is well accepted. The second influences the number of creep sites, not by a relaxation process reducing the number of stress sites, but by a polymerization process similar to well understood chemical processes occurring in gels. The volume changes in C-S-H during this chemical aging process are only moderate. The third involves large dimensional changes in the C-S-H and introduces local high stress regions in the microstructure during changes in relative humidity and temperature.

REFERENCES