



A colloidal interpretation of chemical aging of the C-S-H gel and its effects on the properties of cement paste

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Received 13 October 2004; accepted 14 October 2004

Abstract

The properties, structure, and behavior of cement paste, including surface area, drying shrinkage, creep, and permeability are discussed with the assumption that the C-S-H gel is an aggregation of precipitated, colloidal-sized particles that undergoes chemical aging. A basic thesis of this paper is that C-S-H particles bond together over time, increasing the average degree of polymerization of the silicate chains and causing the C-S-H to become stiffer, stronger, and denser. This process occurs slowly at ambient temperatures, but can be greatly accelerated by elevated temperature curing and is also encouraged 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. The effects of a short heat treatment, which causes rapid aging, depend strongly on the moisture of the paste when it is heated. Many of the observations and insights presented here are not new. The primary objective of this paper is to demonstrate, by reporting a variety of published findings in one place, the significant amount of evidence that has been generated over the past 50 years favoring this interpretation. Another objective is to show that the properties and behavior of the C-S-H gel, and of cement paste, do not require a layered microstructure. Separating chemical aging effects from other changes, such as continued hydration, may well lead to a better understanding of the microstructural causes of creep and shrinkage.

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Keywords: C-S-H; Microstructure; Aging; Physical properties; Modeling

1. Introduction

Recognition of the colloidal and gel-like properties of cement paste, and of the C-S-H¹ component in particular, dates back to the 1950s with the work of Powers and his colleagues at the Portland Cement Association (see for example Ref. [1]). However, during the intervening half-century of research, the colloidal properties of the C-S-H gel have often been 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 models of C-S-H, 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 explored. 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, but it does not address changes that occur in the saturated state.

If the C-S-H in cement paste is a colloidal gel there are important implications for both creep and shrinkage, particularly when combined with the phenomenon of chemical aging. In this context, a detailed definition of aging is

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¹ Cement chemistry notation: C=CaO, S=SiO₂, H=H₂O.

required to avoid confusion. 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. This may not be consistent with definitions in the cement literature, which often equate aging with the slow continued progress of the hydration reactions in mature hardened paste. 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 even as it undergoes loading and/or drying. The properties of cement paste stored under saturated conditions at room temperature continue to change long after the hydration reaction has stopped. In this context, the term aging must include changes due to both increased hydration of the cement particles and changes in the microstructure of the products after they form. These changes include increases in the specific surface area measured by gas sorption, changes to the pore size distribution, and a continued increase in stiffness.

As developed by Bazant et al., models of creep and shrinkage of cement paste predict that the response of a paste to loading or drying will continue to change long after the hydration reaction has stopped (see for example Refs. [4–6]). Perhaps the most sophisticated mathematical theory of creep relies on the concept of microprestresses [6], which are attributed to volume changes as hydration product forms, as well as to changes in disjoining pressure. Increased stress at these “creep sites” increases the ease of bond breakage, thereby increasing the creep rate. According to this theory, freshly produced hydration product contains a relatively high density of these sites, but over time the stresses relax, thereby 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 that large internal stresses are formed during hydration. C-S-H forms under near-equilibrium conditions with respect to the aqueous phase [7], making it unlikely that high internal stresses that could act as creep sites would develop.

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 increased relative to paste hydrated 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 constant high-temperature curing [8,9].

A recently proposed model for the structure of the C-S-H gel [10] considers the C-S-H in cement paste to consist of

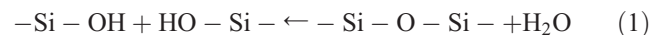
aggregations of roughly equiaxed colloidal-scale particles with no long-range layered structure on a scale greater than a few nanometers. This model rationalizes a variety of published observations and measurements, allowing specific surface area, density, and composition to be predicted as functions of water content or relative humidity (RH). Although the 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 of 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 sintered into a dense body. Applications of sol gel processing include the production of porous membranes, sensors, insulation, optical and protective films, and bulk optical glass. Although sol–gel processing has been practiced 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 [11].

The increased use of sol-gel processing 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 that was not available to earlier cement researchers. The valuable book by Brinker and Scherer [11] 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, a reaction called condensation. In its simplest form, the condensation reaction can be written as



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, as illustrated by Fig. 1. 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, which

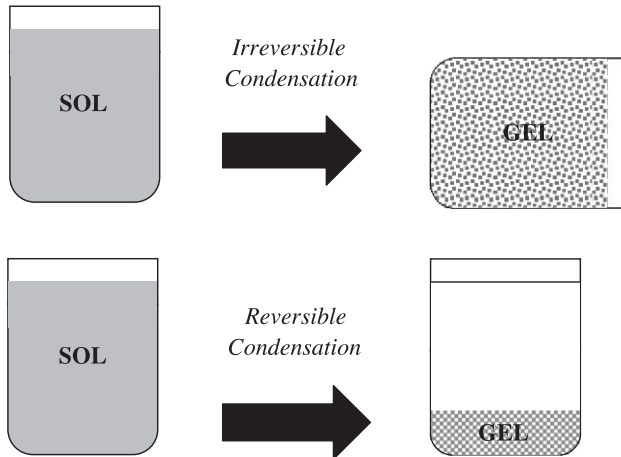


Fig. 1. The sol–gel transition, driven by reversible and irreversible condensation reactions. Reversible condensation leads to a denser gel.

form more polymers they also restructure and reorganize themselves, creating more and more cross-links and becoming increasingly dense. Eventually, solid, dense particles are formed that occupy only a small fraction of the original sol volume.

Under conditions intermediate between the reversible and irreversible 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 [12], the C-S-H phase of cement paste 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 a large free energy change causes the reaction to be very rapid, 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 of gels is generally an increase in the strength and stiffness [11]. 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. Colloid model for the structure of C-S-H

A model for the structure of C-S-H has been proposed [10] that quantitatively rationalizes numerous experimental observations, including surface areas measured by different techniques, densities at various water contents, observed microstructures, C-S-H particle size as measured by neutron scattering (globules), and fractal structure. The C-S-H in cement paste forms with two packing densities, corresponding to high-density (HD) and low-density (LD) morphologies (see Fig. 2). Table 1 compares some of the experimental and modeled values for density, surface area, and porosity at various water contents.

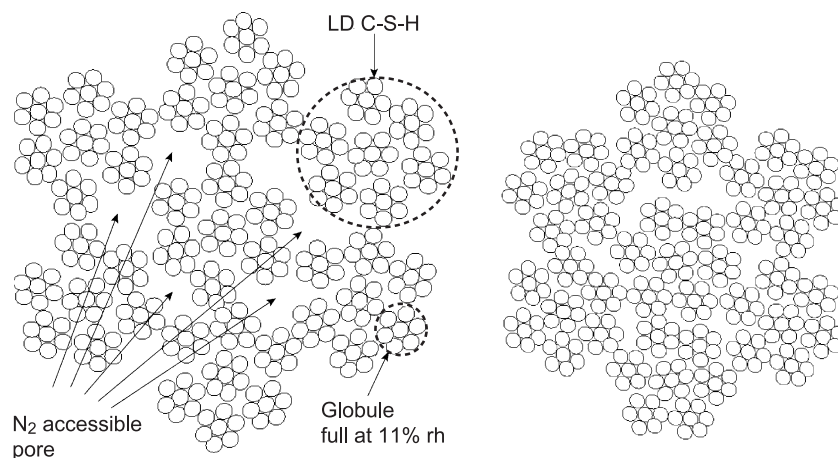


Fig. 2. Schematic representation of low-density (LD) C-S-H (left) and high-density (HD) C-S-H (right), according to the model of Ref. [10].

Table 1
Water content and density of C-S-H as predicted by the quantitative colloidal model of C-S-H

Name of unit in structure	Radius ^a of unit (nm)	Computed density ^b (kg m ⁻³)		Surface area (m ² g ⁻¹ of C-S-H)	Model porosity ^c (%)	Relative humidity condition	Measured composition	Measured density (kg m ⁻³)	Porosity based on composition ^d (%)
		Pores empty	Pores full						
Basic building block	1.1	2800	2800	1000 ^e	–	Dry	1.7CaO · SiO ₂ · 1.4H ₂ O	2800	0
Globules	2.8	2300	2480	460 ^f	18	11%	1.7CaO · SiO ₂ · 2.1H ₂ O	2450	16
LD	8.3	1440 ^g	1930	250 ^g	49	Saturated	1.7CaO · SiO ₂ · 4.0H ₂ O	2000	42
HD	>100	1750 ^g	2130	0	38	Saturated	1.7CaO · SiO ₂ · 4.0H ₂ O	2000	42

^a Assuming spherical particles; using relation, $r=3/(SSA \cdot \rho)$ where r =radius, SSA =specific surface area, and ρ =density.

^b Based on volume fraction of solid and pores.

^c Calculated as $(1-\rho_{\text{unit}}/\rho_{\text{basic building block}}) \cdot 100$.

^d Computed from the molar volume of dry C-S-H and the molar volume of water. The molar volume of dry C-S-H (1.7CaO · SiO₂ · 1.4H₂O) was computed by dividing the molecular weight by the measured density to obtain a value of $6.45 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. The molar volume of water was taken to be $1.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$.

^e Based on SAXS data.

^f Based on SANS data, assuming that only the LD C-S-H structure contributes to the surface area.

^g Values were optimized by maximizing the statistical fit between reported values of nitrogen surface areas, pore volumes and capillary porosity with predicted values of the model.

According to the model the smallest unit of C-S-H is a small tobermorite-like or jennite-like particle. These fundamental units are packed together irregularly into structures called globules, and globules are packed together to form LD and HD structures. The spaces between the smallest units are analogous to the interlayer space in layer-based models [2,13]. The spaces between the globules are the gel porosity that is intrinsic to C-S-H. The spaces between the LD and HD particles are large gel pores that might be considered small capillary pores in other models [14].

Different techniques for measuring surface area probe the structure of C-S-H at different resolutions and, due to the fractal nature of the C-S-H structure, they provide correspondingly different surface area values. With the modeled structure, the surface areas are computed from the size of a sphere with a diameter that represents the length scale of a saturated unit at a particular relative humidity, as listed in Table 1. The experimentally measured value of the C-S-H fractal dimension agrees very well with the value computed from the model structure [10]. While this model is successful from the point of view of explaining disparate measurements, the deformation behavior of the C-S-H during loading and drying has not been addressed. Parts of the remainder of this paper are an effort to start modeling the deformation process.

5. Aging and the structure of cement paste

The degree of polymerization of the silicates in cement paste has been roughly measured by the trimethylsilylation method and accurately measured by ²⁹Si NMR. Results have shown that there is a progressive polymerization of the silicate with time, and that this process is greatly accelerated by increase in temperature [13]. Fig. 3 shows both the progression of polymerization during hydration and the

increase in the rate and degree of polymerization at higher temperature [15]. These results establish that C-S-H undergoes chemical aging, and this is completely consistent with the hypothesis that C-S-H is a colloid.

Because cement paste contains significant amounts of non-gel phases that act as 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 [16]. After set, macroscopic shrinkage of the paste via syneresis does not occur.

There is evidence that drying causes an increase in polymerization [17,18]. Bentur et al. [17] found that in both young and old alite pastes, drying to 52% RH increased the nonvolatile fraction of the derivatized silicates significantly.

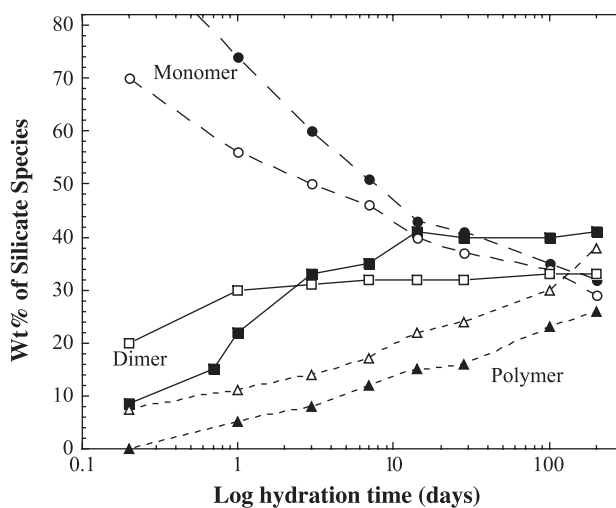


Fig. 3. Weight percent of silicate species present as monomer, dimer, and polymer, as a function of hydration time and temperature, after Ref. [15]. Closed symbols: 25 °C; open symbols: 65 °C.

Table 2
Silicate polymerization and specific surface area in C₃S pastes as a function of age, loading, and drying

	Control	Loaded	Dried	Loaded and dried
<i>Polymerization^a</i>				
Young paste ^b	8	10	18 (53% RH) 21 (11% RH)	13
Mature paste ^c	27	25	13	10
<i>Surface Area (m² g⁻¹)^d</i>				
Young paste ^b	27	21	25	26
Mature paste ^c	21	38	19	25

Data taken from Ref. [17].

^a Percentage of silicate in chains longer than dimers.

^b Approximately 40% hydrated.

^c Approximately 80% hydrated.

^d Measured by nitrogen BET.

Table 2 shows that drying, loading, and hydration temperature influenced the polymerization process according to this study. Another study [19] found no effect of drying on the silicate bonding, so some of these conclusions remain an open subject of research.

Due to the lowering of the activation energy at higher temperatures for condensation of the silicates, aging processes in cement are particularly apparent when comparing pastes with different temperature histories. Hydration of cement at higher temperatures is known to coarsen the pore structure. Although the total amount porosity was unaffected, paste hydrated at 65 °C was found to have a larger capillary pore volume and correspondingly smaller volumes of mesopores (3–30 nm) and micropores (<3 nm) than paste hydrated at 25 °C with the same degree of reaction [20]. The surface area is also lowered by high-temperature curing [21,22]. SEM studies have shown that the layer of hydration product is denser after high temperature curing [23], and that the paste–aggregate interface in concrete is more porous [24]. These physical changes can all be related to aging: the density of the C-S-H gel phase is increased at higher temperatures due to an increased rate of condensation within the precipitated particles. Because the condensation reaction releases a water molecule, it would be expected that the bound water content of C-S-H would decrease with aging, and, in fact, Bentur et al. [21] found that the H/S molar ratio of C-S-H formed at 65 °C was lower than the ratio formed at 25 °C.

6. Effects of aging on the properties of cement paste

6.1. Surface area

The surface area of cement paste as measured by nitrogen gas sorption is influenced by the method used to remove the water from the pores prior to the measurement. A lower surface area can clearly be associated with a compaction, or collapse, of the C-S-H gel, and an associated reduction in the pores accessible to nitrogen. Parrott et al. [25] found that

the largest decrease in surface area was obtained when drying to intermediate humidity levels close to 50%, where capillary stresses are greatest. Further evidence that capillary stresses are responsible for the reduction in surface area comes from the fact that solvent exchange and evaporation, instead of directly drying, significantly increases the nitrogen surface area, and that rapid drying results in higher surface areas than does slow drying.

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% [26]. However, when the surface area is measured by small-angle neutron scattering (SANS), the surface area is virtually unchanged [27]. 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.

Differences between the surface areas measured by nitrogen gas sorption and by SANS are also apparent when measuring the kinetics of surface area formation. The nitrogen surface area increases rather slowly over time, while the SANS surface area increases very rapidly during the first 24 h of hydration and then levels off [28]. This is a reasonable result because the C-S-H formed at early hydration times has a high intrinsic surface area but is particularly susceptible to collapse on drying. Thus, much of the increase in surface area over time with nitrogen is actually an increase in the ability of the C-S-H to withstand drying; that is, an increase in aging.

6.2. 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. These changes are generally considered to be a rearrangement of the C-S-H gel particles on drying, and must be associated with permanent changes in the packing density.

Aging of cement paste reduces the total amount of shrinkage on drying; that is, older pastes and pastes hydrated at elevated temperatures shrink less on drying to a given RH. The irreversible component of shrinkage is affected most strongly by aging. As was first noted by Parrott [8,9], application of a short heat treatment at 60

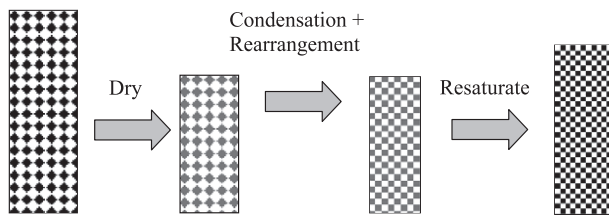
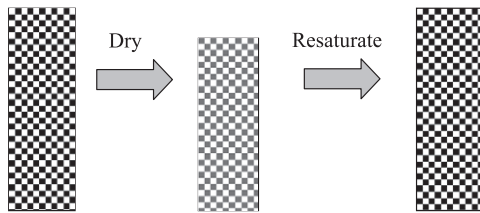
Unaged paste**Aged paste**

Fig. 4. Schematic showing the mechanism for the reduction in irreversible drying shrinkage as cement paste ages. The more stable C-S-H structure of aged paste is illustrated by a finer checkerboard pattern. Dimensional changes are exaggerated.

°C to cement paste also reduces subsequent irreversible drying shrinkage. Under some conditions, a heat treatment at 65 °C can reduce irreversible shrinkage by two thirds [14].

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 [20] 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 [8] found that the weight loss on drying from 100% 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 reduction in irreversible shrinkage with aging indicates that the C-S-H gel becomes less susceptible to collapse or rearrangement as

it ages. The known behavior of pure inorganic gels [11] suggests an explanation, which is shown schematically in Fig. 4. 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 of C-S-H [10] 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 to 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 [17]. One is left with the interesting conclusion that the drying process itself causes aging of cement paste.

Some recent results on heat treating cement paste [29] are included in Table 3. These results show that heating a saturated paste to 60 °C prior to drying reduces the subsequent irreversible drying shrinkage, as expected, but that heat treating the paste when already dry greatly increases the irreversible shrinkage. The rapid aging of the C-S-H induced by heating causes the structure to be strengthened by additional silicate bonding. Thus, when a dry paste is heat-treated, the compression of the C-S-H structure induced by capillary stresses is “locked in” and this essentially converts reversible shrinkage into irreversible shrinkage.

Table 3

Effect of heat treatment^a before and after drying to 50% RH on the shrinkage behavior of cement paste^b

	Drying shrinkage (%)	
	Total	Irreversible
No heat treatment	0.26	0.06
Heat treatment before drying	0.26	0.03
Heat treatment after drying	0.21	0.11

^a 24 h at 60 °C. Dry paste was sealed to prevent any further drying.

^b Data taken from Ref. [29].

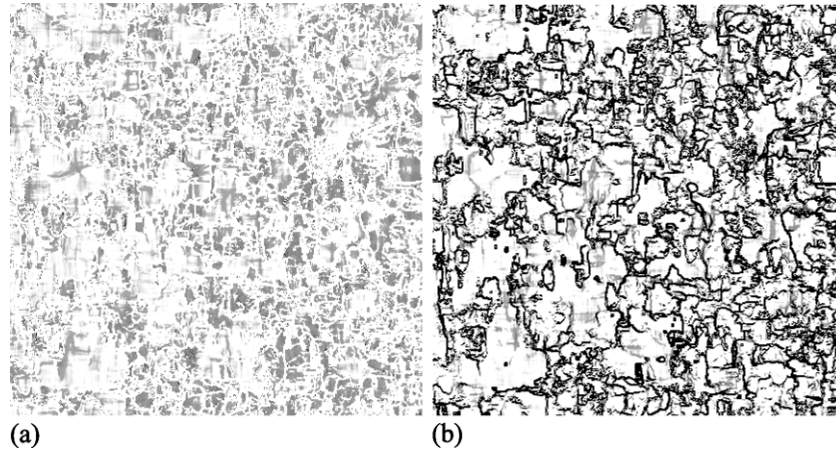


Fig. 5. Deformation maps of the microstructure of a 3-day-old cement paste with $w/c=0.4$, dried to 50% RH. The maps shown above were created using the Deformation Mapping Technique discussed in the text, using digital ESEM micrographs taken at $400\times$ magnification as input: (a) compactions (contraction); (b) rarefactions (expansion) [30].

6.3. 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. When C-S-H is subjected to drying, it could easily experience the conditions that could produce the microprestress sites proposed by Bazant et al. [5]. This is particularly true if C-S-H is mixed with fine material that acts as a restraint to deformation as is 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 this 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. This is called the Deformation Mapping Technique (DMT), and it has been used to measure local deformations as cement paste dries [30]. 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 such as age and initial water-to-cement ratio of the paste. Fig. 5 shows an example of the DMT applied to measuring deformation of a paste that has been dried to 50%

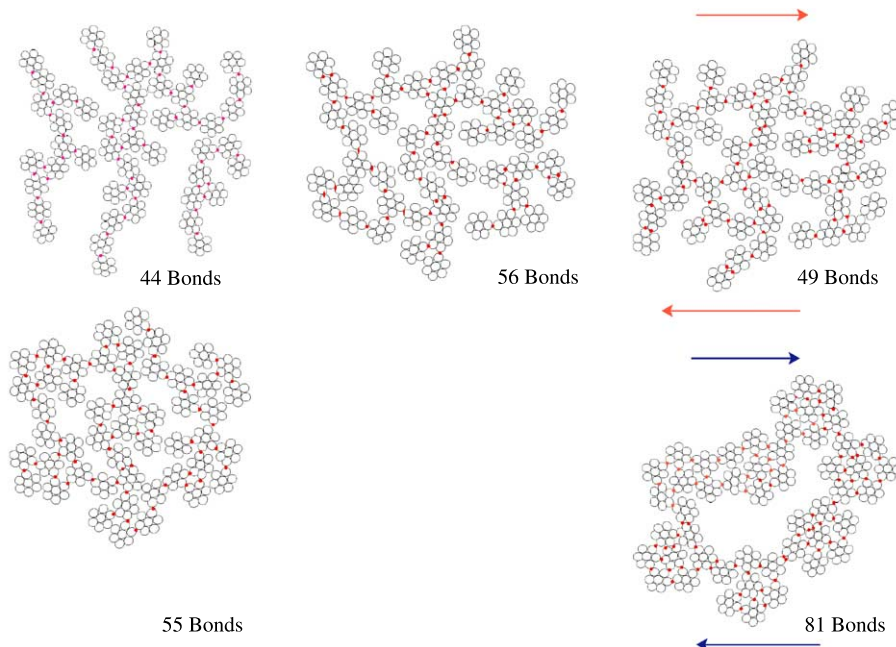


Fig. 6. Model of C-S-H. The top row represents deformation resulting from movement of globules (7 circles in plane section). The bottom row represents deformation by moving low-density units (7 globules in plane section) [31].

relative humidity. As can be seen, very large local deformations, both expanding and contracting, are generated throughout the microstructure by drying. High local stress may result from drying, but this mechanism would not apply to aging in fully saturated cement paste.

Fig. 6 shows a first attempt [31] to model some of the changes to the C-S-H structure that occur on drying, aging, and loading using the C-S-H colloid model of Ref. [10]. Fig. 6 can be loosely compared to Table 3. The structure of wet, early age C-S-H is at the upper left and, as it is subjected to stress (drying or loading), the structure changes as shown in the middle and right diagrams. In this case, the circular units referred to as globules were allowed to move and rotate if there were two bonds or less to nearest neighbors. Drying increased the number of bonds, but no further increase occurred by application of a stress. Moving to the lower level, aging consolidates the LD C-S-H in a mature paste. Deformation now occurs by moving and rotating LD C-S-H units according to the same rules described above except that three bonds were allowed to break.

Both the number of bonds and the surface area as measured by nitrogen are increased by the application of stress. The number of bonds is directly correlated to the degree of silicate polymerization. This is a rough two-dimensional representation, which has promise for quantitatively modeling creep and shrinkage in cement paste. The number of bonds may be related to the ease of creep and be part of the physical explanation for creep sites. One might suggest the density of creep sites is equal to the density of bonds that do not allow creep at a particular load minus the actual density of bonds (which is a function of time, temperature, load history, and relative humidity).

7. 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 process 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. These processes play an important role in the creep and shrinkage of LD C-S-H. The rest of the phases in cement paste act as restraining phases, preventing dimensional changes during aging when no external stress is applied.

Acknowledgement

This work was supported by the National Science Foundation under Contract CMS-007-092.

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