Colloid model of C-S-H and implications to the problem of creep and shrinkage

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ABSTRACT

A model for the structure of calcium silicate hydrate (C-S-H) at the nanometer level (hereafter referred to as "nanometer structure") is described, along with its possible contribution to the understanding of the mechanisms of drying shrinkage and creep in cement paste. The model was developed in two stages and describes C-S-H gel as an aggregation of precipitated, colloidal-sized particles. It was developed in an attempt to account for a number of physical characteristics of C-S-H in mature pastes, including density, surface area, fractal character, pore structure and size of individual particles. In this article the model is extended to include an hypothesis for the mechanisms of viscous deformation under load and/or during drying. As with the original model, the extension proposed here is intended to explain as much apparently unrelated data as possible. Aging (the part unrelated to the increasing amount of hydration products with time) is a process of increasing the number of bonds between globules of C-S-H, causing the C-S-H to become stiffer, stronger, and denser. We propose that deformation is the result of the globules moving under stress or drying, but the mechanism or type of rearrangement of the C-S-H particles [globules] depends on age and on whether or not the sample is dried or loaded or both.

RÉSUMÉ

Est ici décrit un modèle de structure d'hydrate de silicate de calcium au niveau du nanomètre (ci-après désigné sous le nom de structure nanomètre), et sa contribution possible à la compréhension des mécanismes du retrait dû au séchage, et du fluage de la pâte de ciment. Le modèle a été développé en deux étapes et décrit le gel de C-S-H comme un agrégat des particules précipitées et de taille colloïdale. Il a été développé afin d'essayer d'expliquer un certain nombre de caractéristiques physiques du C-S-H dans les pâtes matures, incluant la densité, la surface, le caractère fractal, la structure des pores et la taille des particules individuelles. Dans cet article, le modèle est élargi pour inclure une hypothèse sur les mécanismes de la déformation visqueuse sous charge et/ou pendant le séchage. Comme avec le modèle original, l'extension proposée ici ambitionne de donner une explication à autant de données non reliées que possible. Le vieillissement (la partie non liée à la quantité croissante de produits d'hydratation dans le temps) est un processus d'augmentation du nombre de liaisons entre les globules de C-S-H, permettant au C-S-H de devenir plus raide, plus fort, et plus dense. Nous suggérons que la déformation soit le résultat du déplacement des globules sous la contrainte ou le séchage, mais le mécanisme ou le type de remise en ordre des particules de C-S-H [globules] dépend de l'âge et du fait que l'échantillon soit séché ou compressé ou bien les deux à la fois.

1. INTRODUCTION

1.1 Short history of models

Over the last 50 years, several models for the structure of C-S-H* have been proposed, as summarized in Table 1. 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 (See for example [1, 2]). However, during the intervening years, both chemical and physical arguments were advanced emphasizing that C-S-H has a layered structure similar to tobermorite and jennite [3-5]. The "interlayer spaces" in the C-S-H gel contain water that is removed on drying and re-enters on rewetting, causing shrinkage and swelling [6]. These models have been fairly

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* *Cement chemistry notation:* $C = CaO$, $S = SiO_2$, $H = H_2O$.

Table 1 - Summary of models for the nanometer structure of C-S-H			
Authors	Primary Experimental Basis	Type	Selected Characteristics
Powers (1958)	Water sorption Volume of pores	Colloid	All products of gel particles Gel pore volume 28%
Kantro, Brunauer, Weiss (1970)	Hysteresis of water sorption	Layer Tobomorite	High surface area gel
Feldman Sereda (1970)	Nitrogen sorption Length vs. RH Modulus vs RH Weight vs RH	Layers	Clay-like structure with important role of interlayer water
Wittmann (1979)	Modulus vs RH	Colloid	Important role of water in spaces between particles
Jennings (2000)	Density Composition Surface area Fractal	Colloid	Reconcile as many different physical characteristics as possible

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 developed by Wittmann [7] 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 or irreversible changes that occur under load and/or during drying. Recently the writer and co workers [8-11] have advanced a model, which is an extension of the above models, with emphasis on the colloid nature of C-S-H in the scale range of approximately 1-100 nm. Below this scale, the layer structure seems perfectly valid. Analogies to tobermorite and jennite have also led to a deeper understanding of the atomic structure of C-S-H, including the observed Ca/Si and the chain length of the silicates [12].

In cement paste, C-S-H always forms with an intrinsic pore system, the so-called gel pores, and, therefore, all models of the nanometer structure must account for an extremely high surface area and associated significant volume of tiny pores. Water molecules exist in all of the pores, including the very smallest nanometer-sized pores. Water is an important part of the microstructure since its removal from the smallest pores during drying causes shrinkage and its presence in the smallest pores is necessary for creep under load [13]. These are important observations which help to understand the mechanisms leading to visco-elasticity, a property that is very complex and depends on many parameters, including the age of the sample, rate of drying, temperature history during hydration, and whether or not drying and load are applied simultaneously. Essentially all proposed mechanisms are qualitative and cannot be tested directly through examination of the microstructure. The layer models have generally focused on chemical and physical changes in the structure of the interlayer space. This paper examines a colloid model of the nanostructure of C-S-H with the goal of establishing a quantitative mechanistic understanding of deformation.

1.2 Models and materials science

An important paradigm in materials science is to quantitatively evaluate microstructure in order to make a mechanistic link between processing and properties. In cements the most well understood microstructural feature is the larger "capillary" porosity, controlled primarily by percent reacted and by water/cement. The microstructure has heretofore not been quantitatively evaluated at the length scales that control visco-elastic properties such as creep and shrinkage.

With the goal of understanding several physical properties of C-S-H, a detailed colloid model was proposed a few years ago [8-11]. It is reviewed here with emphasis on certain experimental observations that must be explained by any successful nano-scale quantitative model. Then several striking but preliminary experimental observations about creep and shrinkage are described, followed by a proposed extension of the model.

The microstructure of a material can be characterized in a number of ways. For colloids, the specific surface area has important relationships to many properties. However, for C-S-H the value of the surface area depends on the technique used to measure it, and for BET sorption, the value also depends on the sorbate. When nitrogen sorption is used, the measured surface area depends on other variables, most notably the method used to dry the sample during preparation for analysis. It should be pointed out that some investigators consider the variability of surface area values obtained by nitrogen sorption to be random and not a measure of true surface area or any important aspect of the microstructure. It has been argued that nitrogen does not and can not measure the true surface area because it can not enter the smallest pores, and that the entrance passages are simply too sensitive to factors such as the drying technique and even the age of the sample. It is important to state that the colloid model described here does not suggest that nitrogen measures the total surface area, but rather that it provides information about the stiffness or collapsibility of the C-S-H structure and also provides specific information about the amount of C-S-H having relatively open porosity.

2. COLLOID MODEL

A quantitative model for the structure of C-S-H has been proposed [8-11]. In this present paper, we first give a summary, with emphasis on how the model was validated and on the aspects of the model that may be important to visco-elastic behavior. This is followed by a proposed extension of the model that may lend insight to viscous deformation of young and mature cement pastes.

2.1 Two stage development

The present colloid model was developed in two stages. First [8, 9] the concept of two distinct densities of C-S-H

was introduced to explain the values of the surface area and pore volume of mature samples as measured by nitrogen sorption. Then there followed the publication of a model for the internal structure that reconciled the variation in the values for surface area as measured by a number of techniques; density with different water contents; volume and size of the nanopores; and fractal dimension. Since the original paper, the colloid model has been extended to explain a number of phenomena, including some preliminary ideas about the relationship of aging gels and viscoelastic behavior of concrete [14, 15].

Two densities

The requirement for two densities of C-S-H, low density (LD C-S-H) and high density (HD C-S-H), can be understood in terms of a thought experiment, which first attempts to model C-S-H with a simpler assumption. Because data must be obtained from a number of different samples with different volumes of capillary pores, controlled mainly by the original water/cement ratios, the thought experiment must be carefully–conceived to allow available data to be useful. First, the thought experiment outlines a microstructural explanation for various observed surface areas. This common line of thinking has been generally accepted as the most obvious explanation for various observations, however, it has not succeeded in accounting for a variety of physical characteristics of C-S-H, and, moreover, it leads to conclusions directly contrary to one particular set of measurements, as will be described below.

As already stated, the surface area as measured by nitrogen sorption, S_{N2}, varies significantly. For example higher values are obtained when gentle drying is used to prepare a sample, and lower values with harsher drying. Also, when smaller molecules (such as water) are used for sorption, the values for the surface areas are greater than when larger molecules are used. During the 1960s, the issue of surface area was debated vigorously. Some investigators thought that nitrogen correctly measured the surface area whereas water sorption overestimated the value because it penetrated interlayer spaces (*e.g.* [16, 17]). Others thought that water measured the correct surface area and that nitrogen was excluded from the smallest pores because of "ink bottle" entrances [18-20]. The simplest interpretation of the observations is to assume that the structure collapses to different extents with different preparation techniques (*i.e.* gentle to harsh drying), and/or that smaller molecules penetrate into smaller pores, both effects serving to increase the measured surface area. This seems to provide a satisfactory qualitative explanation for the observations, but surface area alone does not provide a sufficient constraint or boundary condition on a quantitative model. In other words, it is impossible to decide whether the lower values for surface areas are due to "ink bottle" entrances to pores or to different roughness of surfaces. Thus, if only the surface data is considered, too many models can fit the facts.

Any quantitative model for determining the surface area of C-S-H should also predict the volume of fine pores penetrated by the relevant molecule, along with other properties such as the volume and size of pores, and the density of the C-S-H both when the pores are empty and when they are full of water. For the volume of small porosity, only data using nitrogen and water for sorption are available in the literature. Water always measures the same

value for surface area, independent of the method of preparation of the sample or other variables such as original water/cement. Nitrogen sorption is unique in that it both measures a broad range of surface areas and also has yielded some published data for the associated pore volume. Thus, for nitrogen sorption, there should be some sort of direct relationship between surface area and the volume of penetrated gel pores. During the 1960s, carefully D-dried samples that were typically many months or years old were studied in an attempt to determine the "true" surface area and pore volume. Nitrogen and water produced different values and a resulting intense debate [17, 20], but without definitive conclusions. It should be possible to reconcile the various values of surface area with a model.

First, in order to normalize different water/cement ratios, the capillary porosity, which varies over a wide range, must be subtracted, but because of the vague nature of the boundary between capillary porosity and gel porosity, this turns out to be a complex and imprecise task. One way of dealing with different amounts of capillary porosity, and therefore, imprecise information about the volume of gel pores, is to approach the problem from the other end. If the assumption is made that all the porosity is always penetrated by water, then a measure of the volume of gel pores penetrated by nitrogen allows evaluation of the volume of gel pores not penetrated by nitrogen. The difference between the total volume of pores as measured by water sorption and the volume as measured by nitrogen sorption is a value that does not include the capillary pores and a fraction of the gel pores that are larger than a certain size.

This can be expressed as follows. Let G_H = specific volume of gel pores measured by water. (This is the average volume of gel porosity per gram of C-S-H.). Experimentally this is nearly constant, as is the specific surface area measured by water. Since the small gel pores are roughly the same size the following relationship holds:

$$S_N = k \, G_N \qquad (1)$$

where S_N is the specific surface area and G_N is the specific volume of gel porosity of C-S-H measured by nitrogen. The problem is that G_N cannot be measured directly. The total porosity measured by nitrogen, which can be experimentally measured, is:

$$V_N = G_N + C \qquad (2)$$

where C is the capillary porosity, which varies with the initial water/cement ratio and the degree of hydration. The difference between porosity measured by water and by nitrogen is the inaccessible (to nitrogen) pore volume.

$$V_I = G_H - G_N = V_H - V_N \qquad (3)$$

where V_H is the total porosity measured by water. Logically

$$V_H = V_I + G_N + C \qquad (4)$$

$$V_H = G_H + C \qquad (5)$$

from Equation (3)

$$G_N = G_H - V_H + V_N = G_H - V_I \qquad (6)$$

Because surface area as measured by water is constant, G_H must be nearly constant. All of the variables in Equation
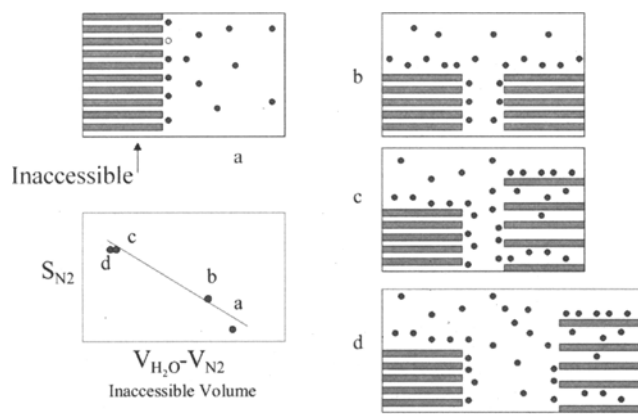
Fig. 1 - Schematic of relationship between the openness of porosity, measured surface area, and volume of pore. When the pore space between the layers is small, a and b, nitrogen cannot enter resulting in a large inaccessible volume and small surface area. If the pores are more open as in c and d, then the inaccessible volume becomes smaller and the surface area becomes greater. In d the large capillary pore is given greater volume than in c but the inaccessible volume remains unchanged.

(6) are either constant or can be measured, and a graph relating V_I to surface area using Equation (1) is shown in Fig. 1. This has generally been the expected trend. The more open the structure, the deeper the nitrogen can penetrate, and the smaller this difference should become.

The limited available data for nitrogen sorption shows a result exactly contrary (and notably linear) to that expected by this model, as shown in Fig. 2. (data taken from [21-23]) This was a major conundrum. Somehow, for nitrogen, the higher the surface area, the greater the volume of pore missed. This puzzle was solved by postulating that there are two types of C-S-H, each with a different density, designated as low density (LD) and high density (HD). The surface of LD particles is accessible to nitrogen but the interior contains a relatively high volume of pores not accessible to nitrogen. The surface of HD is not accessible to nitrogen and the interior contains a smaller volume of pores inaccessible to nitrogen. Thus increasing the amount
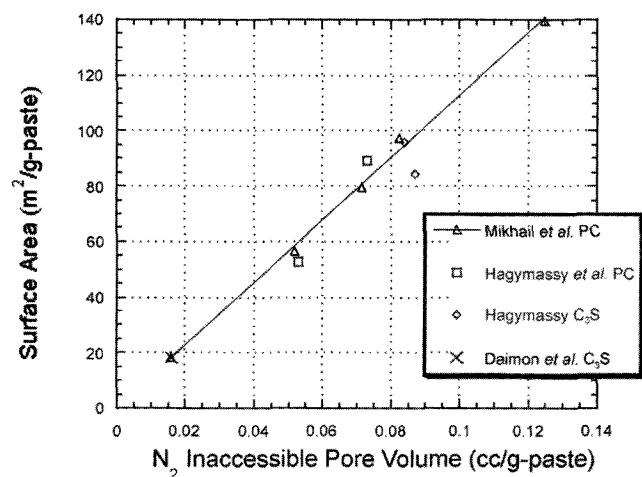

Fig. 2 - The available data strongly contradicts the model described in Fig. 1. Here, the inaccessible pore volume increases with surface area (Data from Mikhail [21], Hagymassy [22], Daimon [23]).
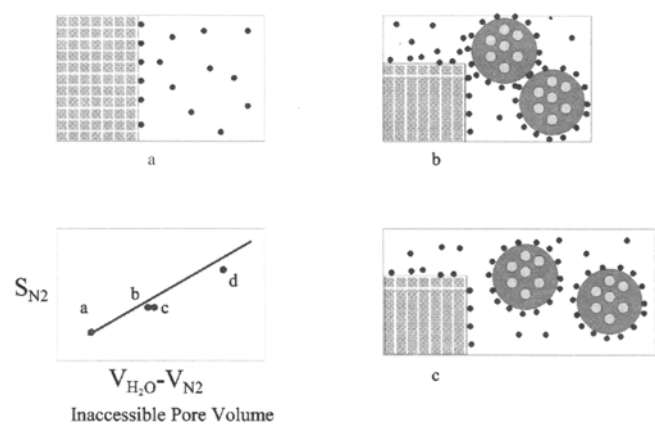

Fig. 3 - Schematic of the proposed model. Surface area as measured by nitrogen increases (b and c are larger than a) when LD C-S-H is formed, shown here as circles, which contain a larger volume of pore that nitrogen cannot enter, compared to the HD C-S-H, shown here as rectangles. Point d is simply an extension of the argument.

of LD C-S-H in a specimen paste has the effect of not only increasing the nitrogen surface area, but also increasing the volume of pores inaccessible to nitrogen, as shown in Fig. 3. A mathematical model for this trend has been published [11].

The model proposes two well-defined densities of C-S-H, the values of which were ascertained by optimizing model predictions with experimental data for mature, D-dried samples. An important point is that the density of C-S-H is defined here as solid C-S-H plus its smallest intrinsic pores. Because the density of solid C-S-H cannot vary much, the two densities result from different volumes of intrinsic porosity. Put another way, this means that there are two packing densities of the tiny C-S-H particles. This does not rule out two ranges of packing densities, especially at younger ages (when the densities could be quite different from the densities of mature samples), but it says that the density is bimodal and only one density contributes to the surface area as measured by nitrogen. This is different than a continuous range of densities that contribute to both surface area and volume of pore in direct proportion to the openness (or inversely proportional to density) of the C-S-H. The above model was based entirely on the volumes of solids and pores, and the specific surface area of C-S-H.

2.2 The colloid structure of C-S-H

The colloid model was developed to explain the structure of the two types of C-S-H. It accounts for different surface areas measured by different techniques; densities and water contents of C-S-H at different RHs; size of particles; size of pores; and fractal dimension.

The starting point was the observation that no matter how it is measured, C-S-H has a high surface area. It is a precipitated colloid (as recently argued by Scherer [24]). Since there is a legitimate analogy between C-S-H and jennite and tobermorite, each having a well defined crystal structure, the small particles must be at least a unit cell in size. Under normal conditions (i.e. at normal temperatures without mineral admixtures, etc.) the small particles aggregate into units that are spherical globules and LD

structures. This aggregation would normally result in syneresis, but in cement paste it occurs in a highly constrained capillary space, which may strongly influence the nanostructure. With this assumption, the mathematical relationship between surface area S, density ρ and radius r or scale is:

$$S = \frac{3}{\rho r} \qquad (7)$$

Fig. 4 shows a two dimensional representation of the packing arrangements of the small particles for LD C-S-H. At progressively increasing length scales the particles pack together with decreasing efficiency up to a length of about 50 nm. The mass fractal dimension 2.73 (as summarized in [10]).

It should be noted that the colloid model is in many ways simply a refinement of the Powers model, which was based on the shapes of the sorption isotherms, much attention being paid to the hysteresis that occurs during sorption and desorption of water and nitrogen. Therefore, the present colloid model should explain these isotherms.

Table 2 shows the computed and experimental values for the density; composition (water content at different RHs); size of particles that contain specific volumes of pores; size of small pores; and specific surface area. The model predicts the experimentally measured values reasonably well, and the validation of the model is simply the broad
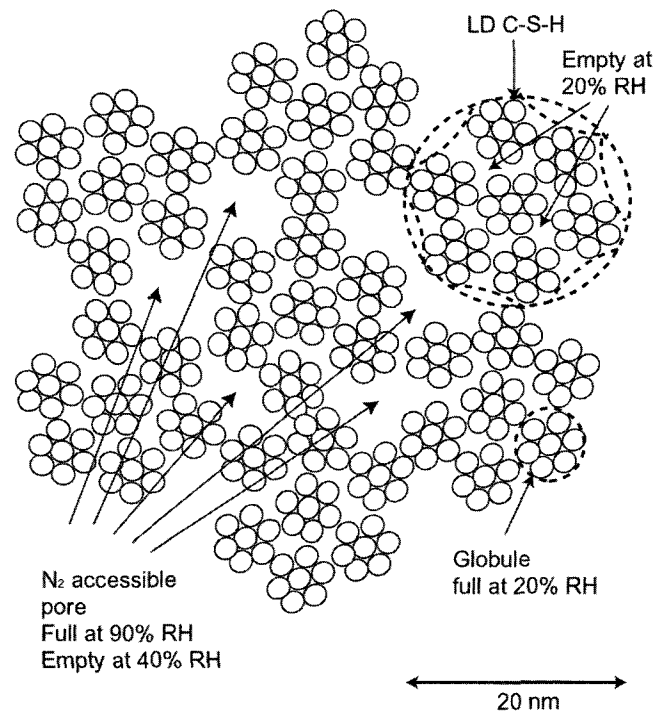

Fig. 4 - Two dimensional schematic of the colloid structure of C-S-H (from [10]). The captions identify the size of unit that is full of water a particular relative humidities.

Table 2 - Predictions of colloid model and measured values for various properties of C-S-H									
Name of unit in structure	Radius[a] of unit (nm)	Computed density[b] (kg m^{-3})		Measured density (kg m^{-3})	Specific surface area (m^2 / g of C-S-H)	Model porosity[c] (%)	Porosity based on composition[d] (%)	Measured composition (RH of measurement)	Pore radius (nm)	
		Pores empty	Pores full						Model Experiment	
Basic Building Block	1.1	2800	2800	2800	1000[f]	-	0 no H$_2$O	1.7 CaO•SiO$_2$•1.4 H$_2$O (Dry — no H$_2$O)	- (i)-	(j)-
Globules	2.8	2300	2480	2450	460[g]	18	16 vol % .7 H$_2$O	1.7 CaO•SiO$_2$•2.1 H$_2$O (11%, .7 H$_2$O)	.24-.45 .17 .24-.45 .5	
LD	8.3	1440[e]	1930		250[e]	49			1.2-1.3	
Average[h]			2030	2000		43.5	42 vol % 2.6 H$_2$O	1.7 CaO•SiO$_2$•4.0 H$_2$O (Saturated, 2.6 H$_2$O)		
HD	>100	1750[e]	2130			0	38		1	
Inter LD									2 .5-5 2.5 10-15 10	

a *Assuming spherical particles; using relation, $r = 3/ (SSA * \rho)$ where r = radius, SSA= specific surface area, and ρ = density.*
b *Based on volume fraction of solid and pores.*
c *Calculated as $(1 - \rho_{unit} / \rho_{basic\ building\ block}) * 100$.*
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 (1.7 CaO•SiO$_2$•1.4H$_2$O) was computed by dividing the molecular weight by the measured density to obtain a value of 6.45 x 10-5 m^3/mol. The molar volume of water was taken to be 1.80 x 10-5 m^3/mol.*
e *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.*
f *Based on SAXS data.*
g *Based on SANS data, assuming that only the LD C-S-H structure contributes to the surface area.*
h *Assuming 50% LD [10] for w/c = 0.5*
i *[25]; j [26]*

agreement between model and experimental values. Some of the values in Table 2 have been published since the model was first published [25, 26].

Comment on the complexity of the Colloid Model

Admittedly, as stated above, the colloid model is more complex than simpler models. It postulates two specific densities with specific pore sizes. This point has been discussed [11]. It is legitimate to note that if some simpler model can make equally accurate predictions, then it should be adopted. However, the unusual results represented in Fig. 2 require a more complex explanation than the more simple assumptions of the past.

The question remains: What chemistry or what mechanisms control the formation of the two densities? The rest of this paper will not answer this question but (1) will explore some of possibilities for variations in the microstructure of C-S-H at early reaction earlier times, and (2) explain how the microstructure might change during drying and/or under load. The goal is to understand aging and its influence on visco-elastic behavior in terms of microstructure.

2.3 Kinetics of reaction and aging

Kinetics

As pointed out in the original paper [10] the globule structure of C-S-H forms primarily during the middle period, between the end of the induction period and the first day or so. This conclusion is based on neutron scattering [27] experiments that measure primarily the surface area of globules. After 24 hrs. the globular structure gradually aggregates into the LD C-S-H structure. After the first day, while the LD structure is still aggregating, the new C-S-H forms primarily with the HD structure directly, without an aggregation process. Furthermore, the LD structure does not form the units described by the model for some time, and the material probably has a much more open structure for a period of many days and months. Thus, not only is the percentage of hydration product increasing, but also the LD C-S-H is undergoing a slow maturation or aging process.

Helperin [26] observed the development of pores size using NMR relaxation techniques, with results shown in Table 2. An interpretation of these results is that this technique measures the formation of LD C-S-H during the first 59 days, and that the capillary porosity is not detected by NMR, probably because these pores are too large. The globules form quickly from newly formed product with internal porosity of radius 2 – 3.8 nm, and the interglobular pores gradually decrease from a radius of about 18 nm to about 12 nm, as the globules aggregate with time. The latter value agrees well with the p value predicted by the model. The NMR results are for saturated samples and therefore, provide some insight about the development of the LD structure.

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 surface area obtained by nitrogen sorption increases rather slowly over time, while the surface area measured by SANS increases very rapidly during the first 24 hrs. of hydration and then levels off [28]. This is a reasonable result in view of the fact that 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 as measured by nitrogen is actually an increase in the ability of the C-S-H to withstand drying, that is, an increase in aging. The SANS data are measured on saturated paste so drying is not an issue. The leveling off of surface occurs as the formation of HD C-S-H, with a low surface area, predominates.

3. VISCO-ELASTIC DEFORMATION AND CHEMICAL AGE

3.1 Aging, sol-gel chemistry and syneresis

Relationship between aging and polymerization of the silicates has been discussed ([29],and reviewed in [30]). There are many similarities between sol – gel processing and the changes that take place as C-S-H forms its colloidal structure.

The key reaction in the aging of silica based gels is the linking of hydrolyzed molecules together, a reaction called condensation. In its simplest form, the condensation reaction can be written as

$$-Si-OH + HO-Si- \leftrightarrow -Si-O-Si- + H_2O \qquad (8)$$

The forward reaction, which liberates water, is the fundamental reaction for linking monomeric species into polymeric clusters, and the reverse reaction, which may be important if a cluster is broken under load, consumes water.

The goal now is to find a way of obtaining and analyzing data so that the mechanisms behind aging and reversible and irreversible drying shrinkage and creep can be understood. This is a challenge because of the limited amount of data, and the complexity of the problem.

The degree of polymerization of the silicates in cement paste has been roughly measured by the trimethylsilylation method and, then more accurately measured by ^{29}Si NMR. Polymerization progresses with time. Furthermore, irreversible creep and drying shrinkage are reduced with age. These results support the possibility that C-S-H ages through a process that bonds the colloid particles together by adding bridging tetrahedra between dimmers. C-S-H contracts, becomes stiffer and stronger with age, a process called syneresis in colloids.

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 [31]. After set, macroscopic shrinkage of the paste via syneresis does not occur under normal conditions. However, decalcification causes polymerization and a large contraction.

3.1.1 Effect of temperature

High temperature curing causes the degree of polymerization of the silicate at a particular age of sample to increase, along with coarsening the pore structure, and lowering the surface area [32]. Although the total amount of porosity is unaffected, paste hydrated at 65°C has 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. A reasonable hypothesis is that 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.

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% [33]. However, when the surface area is measured by small-angle neutron scattering (SANS), the surface area remains virtually unchanged [34]. This anomaly can be explained by remembering that SANS is conducted on a saturated sample, whereas gas sorption requires a drying pre-treatment. Because the heat treatment polymerizes and stiffens the C-S-H phase, it collapses less on drying, thereby allowing more of the internal porosity to be accessed by nitrogen.

3.1.2 Reversible deformation – Elastic deformation

At any age, cement paste exhibits shrinkage due to drying and it creeps under load. The rate at which these effects occur is reduced with time both because of increased degree of hydration (less porosity) and because of chemical aging as described above. Shrinkage and creep have both a reversible and an irreversible component. For drying, most attention has been paid to the mechanisms of reversible shrinkage. For creep, elastic deformation under load is easy to understand, but the mechanisms for the irreversible component are essentially a mystery.

Reversible Shrinkage

There are several different mechanisms by which aging of a gel can affect drying shrinkage. First, the polymerization reactions that constitute aging (Equation (1)) increase the stiffness (modulus) of the gel. Thus, for a given compressive stress the shrinkage strain will be lower after aging. Another effect of aging is a change in 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. Young and colleagues [35, 36] found that a C_3S 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 [29] found that the weight loss on drying from 100% RH 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 as determined from the Kelvin equation (as described in [24]) 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. This was observed directly when a dried sample that was heated to 60°C was observed to expand as the compressive stress was reduced.

The experimental results of Roper [37], summarized in Fig. 5, are often used as a starting point (*i.e.* Mindess and Young [38]) to discuss the mechanisms of shrinkage. The sharp breaks between the different relative humidities are controlled by specific and distinct mechanisms, as summarized in Table 3. However, the relative humidity range at which each mechanism is expected to be most important overlaps these sharp breaks. In other words there

Table 3 - Characteristics of pores in cement paste

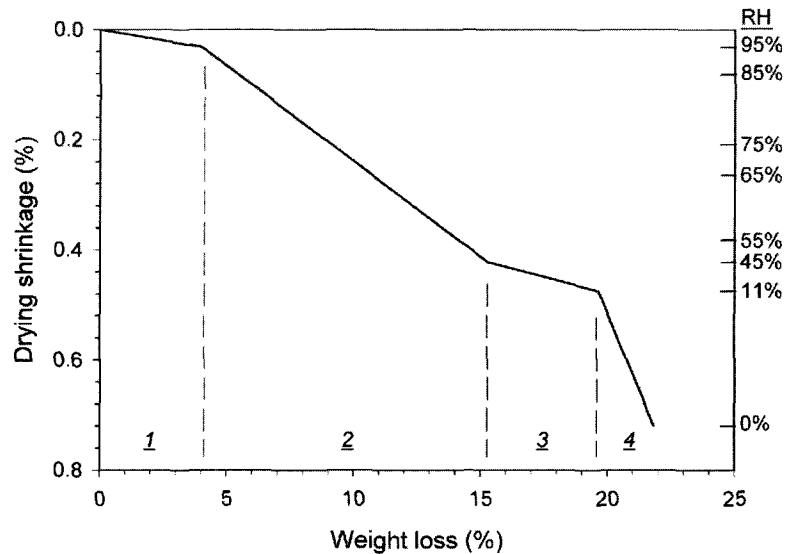| Pore Category	New Pore Category	Size of Pore Within Structure	RH Pores Empty % by Kelvin	Reversible Shrinkage Mechanism
Capillary	Capillary	75nm	90	Capillary Tension
Large Gel Mesopores	Inter LD	2-5	40	Disjoining
Small Gel	Inter-globule	1.2-2	20	Gibbs Bangham
Interlayer	Intra-globule or globule	<.5nm	0	Interlayer

Fig. 5 - This figure shows sharp changes in slope at specific relative humidities (data taken from [37]). The four regions shown here are suggestive of different drying rates exhibited by colloids.

is considerable overlap of one mechanism with another, and the sharp breaks are thus difficult to explain. Also, the mechanisms only account for reversible behavior, whereas, in fact, considerable irreversible shrinkage occurs.

The distinct stages of shrinkage (Fig. 5) can be interpreted in terms of the colloid model. As already discussed the colloid model is able to predict observed specific pore sizes, as opposed to a broad range of pore size. The general openness of C-S-H depends on the length scale. Each scale controls the water content at a specific range of RH's. The Kelvin equation predicts that all the pores greater than a specific pore size (category of pore as referred above), will empty at a relative humidity that is well defined, and therefore the emptying of each size during drying is consistent with the observed changes in slope in Fig. 5. Although details of the mechanisms are expressed somewhat differently here, colloids generally

obey different kinetics on drying at different stages of the drying process [24]. Once again, however, it must be remembered that all of these shrinkage mechanisms are reversible, and that there is also irreversible shrinkage which must be addressed below.

3.2 Microstructure and viscous deformation

Relatively few publications have addressed the problem of microstructural changes that occur during irreversible deformation of C-S-H. Many of the studies cited above report microstructural characteristics, such as degree of polymerization as it is related to the amount of creep or shrinkage that a specimen experiences, without reporting the further changes that occur during creep and shrinkage. Fragments of information are available, but little by way of an organized study. One exception is a 25-year old study reporting results [36] indicating changes in surface area and degree of polymerization for samples subjected to load, drying, and both. These results are summarized in Table 4. Since there have been many technical improvements in instrumentation over the past quarter of a century, these experiments should be repeated and expanded, but for now the major findings serve as a good basis to begin expanding the colloid model to encompass irreversible deformation.

The following is an hypothesis that predicts major trends. There are other changes in the microstructure that can be measured, including the density of the C-S-H at various relative humidities; surface area measured in different ways; size; and shape of globule; and LD structure, as seen by SANS and other characteristics. With further research these changes may be incorporated into the model.

3.2.1 Irreversible drying shrinkage

There is evidence that drying causes an increase in polymerization [39, 40], at least of younger samples. For example, Bentur et al. [36] found that in both young and old alite pastes, drying to 52% RH significantly increased the non-volatile fraction of the derivatized silicates.

According to the colloid model, the C-S-H globules in the LD C-S-H product form fairly quickly, during the first day or so. The structure changes during the ensuing days and months by rearrangement of the globules into the LD structure. Drying provides stresses that pack the globules quicker and more tightly into LD structures. In many ways, drying seems to have effects similar to simple aging. Drying at an early age may cause denser LD structures than aging does over time (structure collapses more).

The schematic in Fig. 6 shows a meniscus that forms around the LD structure at 90% RH. According to the discussion above, this would define the boundary of a capillary pore, and it represents a state that could well be somewhat collapsed from a more open structure that existed before drying from saturation to 90% RH. This is a new way of defining capillary pores, which is predicated on the idea that pores change on drying.

As the RH is lowered, the large meso-gel pores between the LD C-S-H are emptied until at 40% RH the meniscus is just entering the LD structure. The results reported in Table 4 are for samples stored at 52% RH, at which value the LD structure is probably full of water. The right side of Fig. 6 is a hypothetical version of the irreversible deformation that has

occurred on a sample during its first 90 days or so when dried at 52% RH for ten days. The collapse in microstructure is accompanied by a reduction in the nitrogen surface area according to Table 4. As the meniscus enters the inter-LD spaces very large forces develop on the LD structure causing them to pack more tightly.

The value for the surface area of cement paste as measured by nitrogen 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 irreversible collapse of the C-S-H gel, and an associated reduction in the pores accessible to nitrogen. Parrott et al. [41] found that the largest decrease in surface area was obtained after drying to intermediate humidity levels close to 50% RH, at which capillary stresses are greatest. It should be noted that at this RH, water is still in the smallest pores and bond breaking is facilitated by the reverse reaction of Equation (1). At lower RH, the water in the inter-globular spaces has gone up into the smaller pores and bond breaking becomes more difficult, as will be discussed further in the section on creep. These are conditions that produce a dense gel (large driving force of compaction and bond breaking and rearrangement is facilitated). It is interesting that rapid drying results in higher surface areas as measured by sorption than does slow drying.

Table 4 - Silicate polymerization and specific surface area in C₃S pastes as a function of age, loading, and drying. Data taken from [39]

	Polymerization [a]			
	Control	Loaded	Dried	Loaded and Dried
Young paste [b]	8	10	16	13
Mature paste [c]	23	21	25	26
	Surface Area (m²/g) [d]			
	Control	Loaded	Dried	Loaded and Dried
Young paste [b]	27	25	13	10
Mature paste [c]	21	38	19	25
	Irreversible strain x 10⁻⁴			
	Control	Loaded	Dried	Loaded and Dried
Young paste [b]	-	0.6	8.1	16.8
Mature paste [c]	-	2.7	6.8	15.0

(a) *Percentage of silicate in chains longer than dimers.*
(b) *Approximately 40% hydrated.*
(c) *Approximately 80% hydrated.*
(d) *Measured by nitrogen BET.*

This is probably due in part to time dependence of the collapse process but also to the removal of critical bond breaking water.

Fig. 7 shows a schematic of the meniscus entering the C-S-H at the 90% RH. This has the effect of breaking bonds between LD units (inter-LD bonds) and causing the LD units to rearrange so that they are a little more tightly packed.

3.2.2 Irreversible creep

Irreversible deformation of samples saturated with water while under stress (so-called basic creep) involves rearrangement of globules. This is a thermally activated process [42, 43], and data has been interpreted by a rate
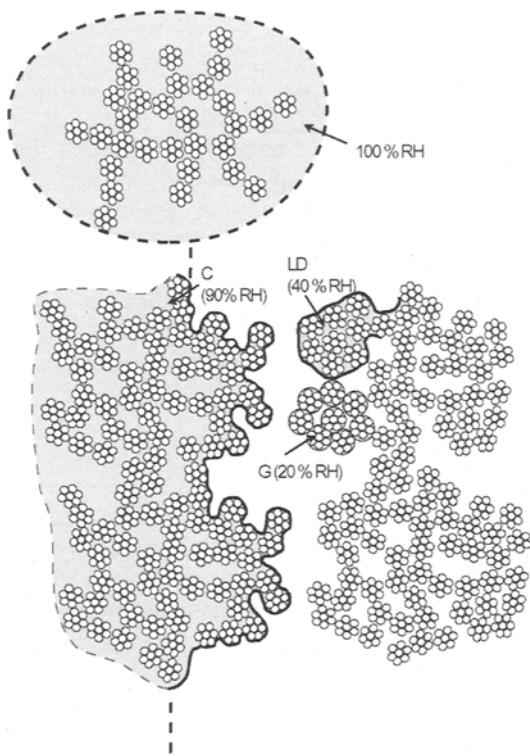
Fig. 6 - Drying C-S-H during the early stages of the aging process. A 90% relative humidity the meniscus is just entering the gel structure. The structure has collapsed from a more open structure shown in the upper left. A 40% RH the LD structure is full of water and at 20% RH the globules are full of water. The bonding increases and the surface area is reduced.
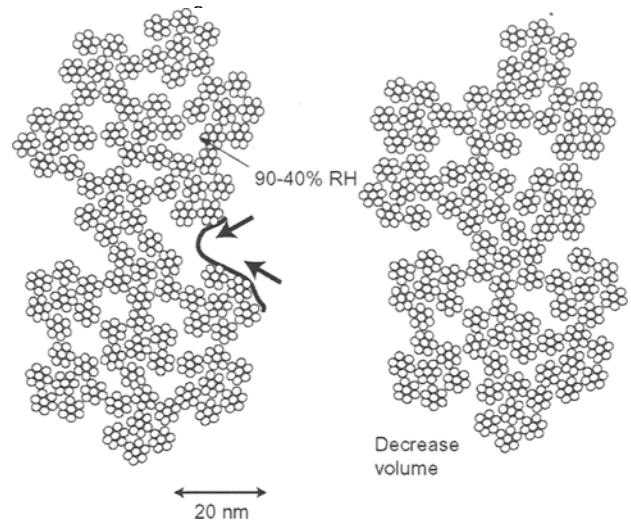

Fig. 7 - Drying of mature C-S-H. As the meniscus enters the C-S-H gel the stress on the LD units are sufficient to break the relatively few near neighbor bonds, resulting in a tighter packing of the LD units. Neither the bonding or the surface area change much during this process.

equation that contains both an activation energy term and an activation volume term. The activation energy increases with age of sample, which results in reduced creep. The activation volume term is unique to a reaction which not only involves activated chemical states but also the physical movement of a mass through a distance, as must be necessary during irreversible creep. The creep rate is described by:

$$\dot{\varepsilon} = a_0 \exp\left(-\frac{Q}{kT}\right) \sinh\left(\frac{V\sigma}{kT}\right) \qquad (9)$$

where Q is the activation energy (which increases with time) and V is the activation volume. The activation volume is multiplied by stress, giving the numerator of the exponent the units of force x distance, *i.e.* work. Thus a cross section of material is moved through a distance. By analyzing data for concrete subjected to various stress and temperatures, values for Q and V can be obtained. The value for V ranges between 4×10^{-20} and 1×10^{-23} cm^3, depending on age and w/c of the sample. With the assumption that the volume has equal dimensions in every direction, a linear dimension of 0.2 to 5 nm is obtained, suggesting that it is a globule that moves.

Plastic deformation generally occurs under the influence of shear stress (as opposed to compressive stress on drying). At young ages there is relatively little irreversible creep. This is probably because the LD structure is relatively open and shear deformation can occur without much rearrangement, as shown in Fig. 8 (this is elastic deformation). As the load is increased, the tensile component becomes large enough to cause rupture before rearrangement can occur. Globules move in younger samples without significantly changing the inter-globular bonding or the surface area as measured by nitrogen sorption.

In addition to the above arguments, of all of the structures at different scales in the colloid model, globules may be the easiest to visualize as moving relatively easily as separate units through the microstructure. Fig. 9 shows possible sequence of movements, starting from left to right, first one globule moves and then another moves into space that opens up. This is a process that is analogous to the movement of a dislocation. In mature samples, globules move with much more difficulty because the structure is more tightly packed and well bonded. In the process of moving, the globules open the structure and increase the surface area. This is because globules in mature paste are more tightly packed than they are in young samples. If the stress is sufficient to break bonds in young samples then overall fracture occurs. In mature samples the near proximity of other globules results in bonds being reformed quickly.

It is well documented that creep is dramatically reduced when samples are dried below about 50% RH. According to the model described here at these low RHs the inter-LD water is removed at 40% RH and the inter-globule water is removed at 20% RH. Removal of water prior to load both collapses the structure, making it more difficult to move globules, and also shifts the equilibrium to the left in Equation (1). Both of these effects make creep more difficult.

3.2.3 Creep and shrinkage

The nonlinear addition of creep and shrinkage has been the subject of much debate. This is often called the Picket effect, and is sometimes explained by introducing the idea that drying probably causes differential shrinkage, because the surface shrinks first, and this causes cracking. If a compressive load is applied during drying, therefore, not only is creep induced but cracking is suppressed. This
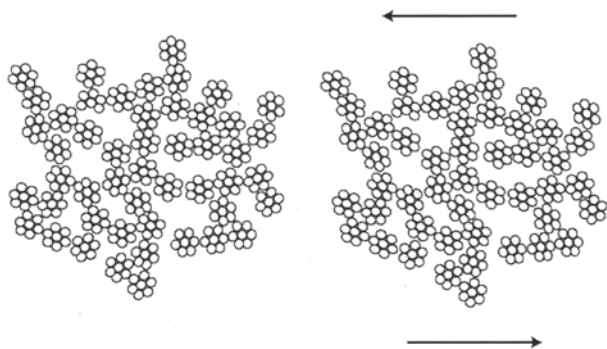
Fig 8 - Creep under shear stress of immature C-S-H, middle stages of aging. Since there are few bonds between near neighbor globules the C-S-H stretches and when the stress is sufficient to break bonds rupture occurs instead of a rearrangement. Irreversible creep is small and neither the bonding or surface area change much.
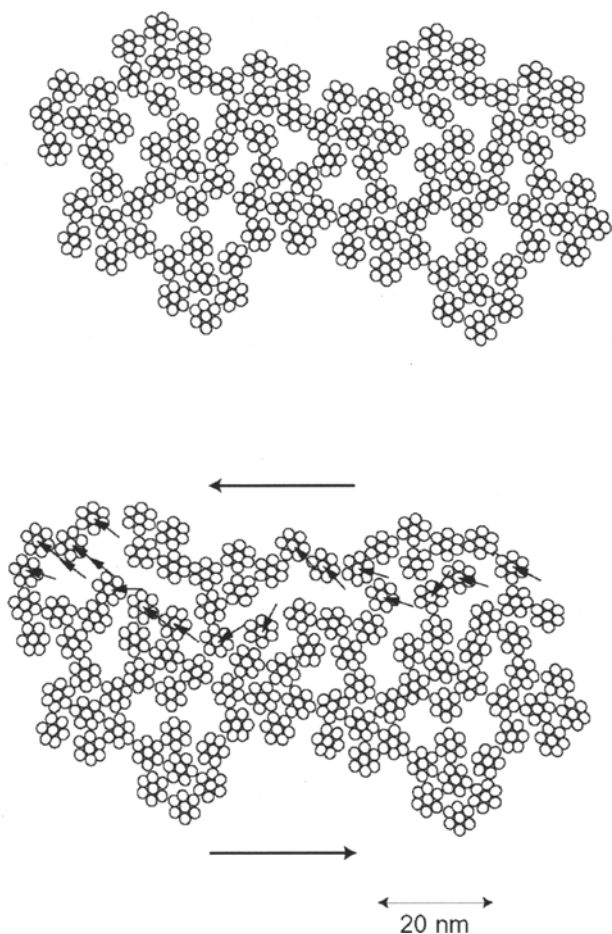

20 nm

Fig 9 - Creep of mature C-S-H. This model suggests a complicated one-at-a-time motion of globules. As one moves a space a space is created, and then another moves into that space. The structure opens, increasing the surface area, although the number of bonds does not change.

removes an expansion, and the overall shrinkage (drying shrinkage plus creep) is increased.

The above discussion suggests quite different mechanisms for creep and shrinkage. According to this model creep is the motion of globules under shear. The packing density and therefore the volume of C-S-H may not change much, or it

may even expand (as suggested by the increase in surface area of mature samples). On the other hand, shrinkage is the tendency to form LD C-S-H with densities different from those described above for well-hydrated samples that have been very carefully dried. The volume of C-S-H should always shrink on drying, the amount depending on age and method of drying. If C-S-H shrinks on drying in a constrained pore space, as can occur in cement paste [44, 45], then the bonds in general will be under tensile stress. The applied load results in shear stress that moves globules. It is easy to imagine that the combination of the load and drying make it much easier to break the bonds to move globules than does either drying or external load applied alone.

3.2.4 General comments

The present understanding of changes in the microstructure of C-S-H is too vague to allow more detailed speculation about the mechanisms that control creep and/or shrinkage. Although degree of polymerization seems to have a direct correlation with aging, the changes that occur during drying and under load are much more complex. Much more research is necessary.

Both irreversible shrinkage and creep are processes that slow down with time. They are modeled here by invoking the motion of LD and globule structures, relating the slowing to some sort of optimum packing. This could have surprising consequences about the rate and extent of strain when the load is reversed. Such a mechanism also provides a ready explanation for the observation that pastes that are repeatedly dried and re-saturated display 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 re-wetting [36]. One is left with the interesting conclusion that the drying process itself causes aging of cement paste.

This paper has discussed a model and speculated mechanisms for deformation at the nano-scale. There are issues of scaling up to the very large sizes of practical concrete. Aggregate generally adds a restraining phase, but at the micron level there are still many questions to be answered. In order to investigate 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 [46]. 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. Concrete shrinks because C-S-H shrinks within a framework of restraining phases.

As for scaling down, the chemical composition and structure of the building blocks must be established. The solubility of C-S-H and the degree of polymerization depends on the chemical characteristics of the basic building blocks [47].

4. SUMMARY

This paper has reviewed the development of the colloid model, which took place in two stages: 1) the concept of two densities and 2) the examination of the detailed structure of the two densities.

Creep and shrinkage are a function of aging of the C-S-H, which not only depends on time, but also on the temperature, relative humidity, and the history of the C-S-H. Aging is a process of polymerization of the silicates in the C-S-H. As C-S-H ages the globules become more tightly packed. Aging is accelerated by drying and by increasing the temperature. These are phenomena that are similar to those in many colloid gels.

An hypothesis for viscous flow has been advanced. The mechanism of deformation depends on age of the C-S-H. The hypothesis separates the mechanisms for deformation under applied stress and deformation due to drying. These are changes that should be detectable by modern methods of measurement.

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REFERENCES

[1] Powers, T.C., 'Physical properties of cement paste', in Fourth International Symposium on the Chemistry of Cement, Washington, D.C., National Bureau of Standards (1960) 577-609.

[2] Powers, T.C. and Brownyard, T.L., 'Studies of the physical properties of hardened Portland cement paste', *PCA Bulletin* **22** (1948).

[3] Kantro, D.L., Brunauer, S. and Weise, C.H., 'Development of surface in the hydration of calcium silicates', in 'Advances in Chemistry Series' (R.F. Gould, Editor, American Chemical Society, Washington, D.C., 1961) 199-219.

[4] Brunauer, S., 'Tobermorite gel - the heart of concrete', *Am. Sci.* **50**(1) (1962) 210-29.

[5] Taylor, H.F.W., 'Hydrated calcium silicates. Part 1. Compound formation at ordinary temperatures', *J. Chem. Soc.* (1950) 3682-90.

[6] Feldman, R.F. and Sereda, P.J., 'A new model of hydrated cement and its practical implications', *Eng. J. Can.* **53** (1970) 53-59.

[7] Wittmann, F.H., 'Trends in research on creep and shrinkage of concrete. in cement production and use' (J. Skalny, New Hampshire, Engineering Foundation - New York, 1979) 143-61.

[8] Jennings, H.M. and Tennis, P.D., Model for the Developing Microstructure in Portland Cement Pastes. *J. Am. Ceram. Soc.* **77**(12) (1994) 3161-72.

[9] Tennis, P.D. and Jennings, H.M., 'A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes', *Cem. Concr. Res.* **30**(6) (2000) 855-63.

[10] Jennings, H.M., 'A model for the microstructure of calcium silicate hydrate in cement paste', *Cem. Concr. Res.* **30** (2000) 101-16.

[11] Jennings, H.M., 'Reply to the discussion of the paper "A model for the microstructure of calcium silicate hydrate in cement paste" by I. Odler', *Cem. Concr. Res.* **30**(8) (2000) 1339-41.

[12] Chen, J.J., Thomas, J.J., Taylor, H.F.W. and Jennings, H.M., 'Solubility and structure of calcium silicate hydrate', submitted to *Cement and Concrete Research* (2003).

[13] Wittmann, F., 'Einfluss des Feuchtigkeitsgehaltes auf das Kriechen des Zementsteines', *Rheol. Acta* **9** (1970) 282-287 [in German].

[14] Thomas, J.J. and Jennings, H.M., 'Effect of heat treatment on the pore structure and drying shrinkage behavior of hydrated cement paste', *J. Am. Ceram. Soc.* **85**(9) (2002) 2293-98.

[15] Thomas, J.J. and Jennings, H.M., 'A colloidal interpretation of chemical aging of the C-S-H and its effects on the properties of cement paste', *Cem. Concr. Res.* (in press).

[16] Feldman, R.F. and Sereda, P.J., 'A new model of hydrated cement and its practical implications', *Eng. J. Can.* **53** (1970) 53-59.

[17] Feldman, R.F., 'The flow of helium into the interlayer spaces of hydrated Portland cement paste', *Cem. Concr. Res.* **1** (1971) 285-300.

[18] Brunauer, S., 'Tobermorite gel - the heart of concrete', *Am. Sci.* **50**(1) (1962) 210-29.

[19] Kantro, D.L., Brunauer, S. and Weise, C.H., 'Development of surface in the hydration of calcium silicates. II: Extension of investigations to earlier and later stages of hydration', *J. Phys. Chem.* **66** (1962) 1804-09.

[20] Brunauer, S., 'A discussion of the helium flow results of R.H. Feldman', *Cem. Concr. Res.* **2**(4) (1972) 489-392.

[21] Mikhail, R.S., Copeland, L.E. and Brunauer, S., 'Pore structures and surface areas of hardened Portland cement pastes by nitrogen adsorption', *Can. J. Chem.* **42** (1964) 426-38.

[22] Hagymassy, J., Odler, I., Yudenfreund, M., Skalny, J. and Brunauer, S., 'Pore structure analysis by water vapor adsorption. III: Analysis of hydrated calcium silicates and Portland cements', *J. Colloid Interface Sci.* **38**(1) (1972) 20-34.

[23] Daimon, M., Abo-El-Enein, S.A., Hosaka, G., Goto, S. and Kondo, R., 'Pore structure in calcium silicate hydrate in hydrated tricalcium silicate', *J. Am. Ceram. Soc.* **60** (1977) 110-14.

[24] Brinker, C.J. and Scherer, G.W., 'Sol-Gel Science' (New York Academic Press, 1990) 908.

[25] Valckenborg, R.M.E., Pel, L. and Kopinga, K., 'Combined NMR cryoporometry and relaxometry', *J. Phys. D. Appl. Phys.* **35** (2002) 249-56.

[26] Halperin, W.P., Jehng, J.Y. and Song, Y.Q., 'Application of spin-spin relaxation to measurement of surface area and pore size distributions in a hydrating cement paste', *Magn. Reson. Imaging* **12**(2) (1994) 169-73.

[27] Allen, A.J., Oberthur, R.C., Pearson, D., Schofield, P. and Wilding, C.R., 'Development of the fine porosity and gel structure of hydrating cement systems', *Phil. Mag. B.* **56**(3) (1987) 263-68.

[28] Thomas, J.J., Jennings, H.M. and Allen, A.J., 'The surface area of cement paste as measured by neutron scattering - Evidence for two C-S-H morphologies', *Cem. Concr. Res.* **28**(6) (1998) 897-905.

[29] Parrott, L.J., 'Basic creep, drying creep, and shrinkage of a mature cement paste after a heat cycle', *Cem. Concr. Res.* **7** (1977) 597-604.

[30] Thomas, J.J. and Jennings, H.M., 'A colloidal interpretation of chemical aging of the C-S-H gel and its effects on the properties of cement paste', *Cem. Concr. Res.* (2003) (in press).

[31] Rooij, M.R.D., 'Syneresis in cement paste systems, in Civil Engineering', Delft University of Technology, Delft 832000.

[32] Bentur, A., 'Effect of curing temperature on the pore structure of tricalcium silicate pastes', *J. Colloid Interface Sci.* **74**(2) (1979) 549-60.

[33] Chen, J.J., Thomas, J.J. and Jennings, H.M., 'Silicate polymerization in calcium silicate hydrate during the decalcification of tricalcium silicate pastes' (in prep.)

[34] Thomas, J.J., Allen, A.J. and Jennings, H.M. (unpublished results).

[35] Mindess, S., Young, J.F. and Lawrence, F.V., 'Creep and drying shrinkage of calcium silicate pastes. I: Specimen preparation and mechanical properties', *Cem. Concr. Res.* **8** (1978) 591-600.

[36] Bentur, A., Milestone, N.B. and Young, J.F., 'Creep and drying shrinkage of calcium siciate pastes. II: Induced microstructural and chemical changes', *Cem. Concr. Res.* **8** (1978) 721-32.

[37] Roper, H., 'Dimensional change and water sorption studies of cement paste', in Symposium on Structure of Portland Cement Paste and Concrete, Washington, D.C., 1966, 74-83.

[38] Mindess, S. and Young, J.F., 'Concrete' (Englewood Cliffs, NJ, Prentice-Hall, 1981) 671.

[39] Bentur, A., Milestone, N.B. and Young, J.F., 'Creep and drying shrinkage of calcium siciate pastes. II: Induced microstructural and chemical changes', *Cem. Concr. Res.* **8** (1978) 721-32.

[40] Milestone, N.B., 'Aging and drying of tricalcium silicate pastes', in Proceedings of the7[th] International Congress on the Chemistry of Cement, Paris, 1980, 61-66.

[41] Parrott, L.J., Hanson, W. and Berger, R.L., 'Effect of first drying on the pore structure of hydrated alite paste', *Cem. Concr. Res.* **10** (1980) 647-55.

[42] Klug, P. and Wittmann, F.H., 'Activation energy and activation volume of creep of hardened cement paste', *Materials Science and Engineering* **15** (1974) 63-66.

[43] Strub, F. and Wittmann, F.H., 'Activation energy and activation volume of compressive and tensile creep of hardened cement paste', in 'Hydraulic Cement Pastes: Their Structure and Properties', Proc. of Conference at Sheffield, 1976, 237-70.

[44] Neubauer, C.M. and Jennings, H.M., 'The use of digital images to determine deformation throughout a microstructure', *J. Mater. Sci.* **35** (2000) 5751 - 65.

[45] Thomas, J.J. and Jennings, H.M., 'Changes in the size of pores during shrinkage (or expansion) of cement paste and concrete', *Cem. Concr. Res.* **33** (2003) 1895-900.

[46] Neubauer, C.M., Garboczi, E.J. and Jennings, H.M., 'Mapping microstructural drying shrinkage deformations in cement-based materials. Part I: Deformation Mapping Technique', *J. Mater. Sci.* **35**(22) (2000) 5741-49.

[47] Chen, J.J., Thomas, J.J., Taylor, H.F.W. and Jennings, H.M., 'Solubility and structure of calcium silicate hydrate', submitted to *Cement and Concrete Research* (2003) (in press).

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