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Relationships Between Microstructure and Creep and Shrinkage of Cement Paste

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"Only by the fusion of science and the humanities can we hope to reach the widsom appropriate to our day and generation."

I.I. Rabi

Creep and shrinkage are reviewed. Both mechanisms and mathematical models are discussed. One of the main points of this review is that progress will be made only when mathematical models are based on a mechanistic understanding, and mechanisms must be related to microstructure.

Introduction

Creep and shrinkage are important material properties that have strong effects on the long-term performance of designed structures. *Creep* is defined as the long-term deformation of a specimen under constant external load. In the case of loading without drying the corresponding deformation is called *basic creep*, in the case of loading and drying simultaneously the deformation is called *drying creep*. *Shrinkage* is the deformation of a specimen during drying without external loading.

Many experiments on creep and shrinkage have been carried out and models have been established to explain the experimental results. However, the mechanisms of creep and shrinkage of cement paste are not yet clearly understood. This can be observed by a historical review of proposed mechanisms, which are characterized by a common feature, that is, each mechanism was plausible when it was proposed, and later it was disproved by new test

results with counterexamples. These complications have prevented a comprehensive model from being developed. Present models will be improved only if a detailed and realistic understanding of microstructure serves as the basis.

The main purpose of this chapter is to give a brief review of creep and shrinkage with emphasis on proposed mechanisms and the material models. First, the chapter will address mechanisms and models for creep, and then mechanisms and models for shrinkage. Creep and shrinkage behaviors are strongly dependent on the microstructural features, so the models for microstructure of cement paste will be presented and the possible links between creep, shrinkage, and the microstructure of cement paste will be explored.

Creep

From the onset it should be noted that both creep and shrinkage should be considered together. This is because creep and shrinkage are coupled in such a way that their combined effect is greater than the sum of the individual effects. This so-called Pickett effect introduces a significant complication to models. Indeed, a complete mathematical description of creep and shrinkage under all drying conditions has not been accomplished.

Both creep and shrinkage are fundamentally measured as strain. One of the following must be important to the mechanism of drying creep:

1. Stress enhances shrinkage possibly by accelerating the transportation of moisture in a specimen.
2. Drying enhances creep.
3. Stress prevents microstructural change, which reduces the strain on drying. In other words, the total shrinkage strain is not measured because of compensation from features such as microcracks.

In addition to the Pickett effect, hysteresis and irreversible strain on rewetting are complex. Irreversible creep involves, probably, relative movements of particles or layers, such as intercrystalline slip and internal rupture of bonds.[1–3] Microcracking, bond breakage, and bond deformation may contribute to creep at high stress and result in nonrecoverable creep. Some important characteristics are illustrated in Fig. 1. Furthermore, all of this behavior is related to rate of change, which, in turn, depends on relative humidity, load, size of specimen, and temperature.[4,5]

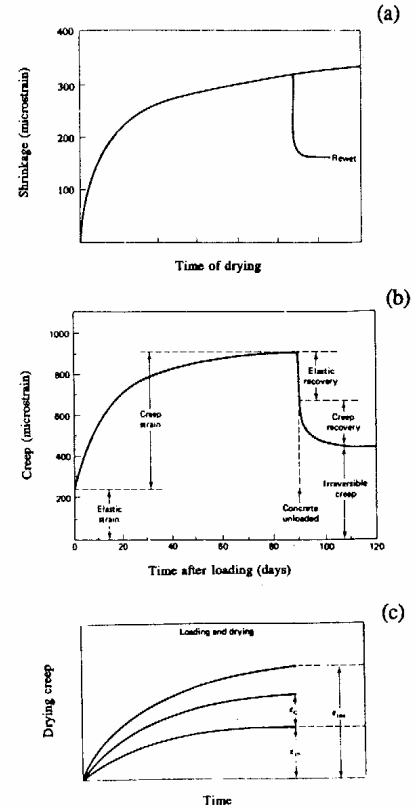

Fig. 1. (*a*) Shrinkage as a function of time in a dry environment followed by rewetting. Time axis does not contain a scale because rate of drying depends on size of specimen. (*b*) Creep deformation as a function of time, and (*c*) strain due to simultaneous loading and drying (E_{tot}) is greater than the sum of shrinkage (ϵ_{sh}) and creep (ϵ_c).

Mechanisms and Models for Creep

With respect to mechanisms for creep, Illston[6] said: "The physical and chemical happenings that are associated with creep are on a molecular scale, and there is no convincing direct evidence of what actually goes on; so the explanation of creep has, perforce, consisted of interpreting engineering-level observations in terms of likely physical and chemical phenomena. This is the way that the creep mechanism game is played, and many research workers in this field have indulged themselves and enjoyed the game." Although Illston is partly correct, the cumulation of knowledge on cement paste is progressing and the basis for comprehensive models is evolving.

Perhaps the earliest theory of creep behavior may be the seepage theory,[7–9] which assumed that creep may be caused by consolidation, like that in clays. Thus, during loading the water within cement paste is squeezed out of the specimen. Only the gel water is involved in the seepage movement; neither the capillary water nor the chemically combined water enter the mechanics. The theory gives an explanation of the large creep of drying concrete compared with wet or dry concrete. However, it was found later that compressive loading results in almost no weight change and that the creep of sealed concrete (basic creep) is important.[10]

Another proposed mechanism, the so-called viscous shear theory,[9,11] suggests that creep is caused by sliding of cement gel particles and that the flux of water through cement paste increases the sliding rate. This idea is shown to be incomplete by the testing specimens through which water permeated at a constant rate; no increase of creep was observed under these conditions.[10]

Another hypothesis is that creep is associated with an aging process of layered material.[12] Creep is considered to be associated with a gradual crystallization, or aging, process of layered material resulting in an increased layering, and that the movement of water is not a major mechanism. The process is associated with either moving together sheets or layers of C-S-H so that the entrance to the interlayer spaces becomes constricted, or the movement of sheets apart from one another to form the new interlayer spaces. Some movement of water must therefore occur as water leaves or enters the interlayer space. Feldman predicted that this further layering or crystallization of C-S-H is the main physical change and thus may be reflected in surface area measurements as measured by gas adsorption isotherms. Later, surface area measurements using nitrogen at various degrees of reaction and various loading and drying conditions showed some changes[2,13] that agree with Feldman's hypothesis; however, the water adsorption showed no change. The proposed reason for this negative result is that drying, a necessary first step for gas adsorption experiments, destroys part of the structure of micropores, but the larger pores are not affected. Furthermore, because interlayer space is not considered part of the pore structure, water that enters the interlayer space renders adsorption using water as an inaccurate measurement. As a result, the change in larger pores induced by loading or drying can be detected only by nitrogen.

Wittmann and others described creep by rate-process with an activation energy.[14–18] This hypothesis is based on the idea that movement of solid particles is responsible for creep, the movement of water is not rate-controlling. The hypothesis states that cement paste contains regions, or elements, where the activation process results in the spontaneous movement of matter to new positions. When there is no preferred direction to the energy potential, activation of creep elements occurs randomly, in all directions. This theory can be expressed mathematically.

$$P = C_a e^{-\frac{Q}{RT}} \tag{1}$$

The probability of a particle to overcome the bond is given where C_a is a constant, Q is activation energy, R is gas constant, and T is absolute temperature. However, when an applied stress is present, activation is biased in the direction of the potential by an amount u (decrease in loading direction and increase in the opposite direction) and the above equation becomes

$$\begin{aligned} P &= C_a e^{-\frac{Q-u}{RT}} - C_a e^{-\frac{Q+u}{RT}} \\ &= 2C_a e^{-\frac{Q}{RT}} \sinh\left(\frac{u}{RT}\right) \end{aligned} \tag{2}$$

and the movement of the material at the macroscale, associated with such an activation, is the cause of creep. u could be assumed to be a linear function of stress σ, $u/RT = A\sigma$, and Q a function of time, $Q(t) = Q_0 + m \ln t$, with A, Q_0, and m as constants. Then the rate of creep may be written in the same form and the following expression can be obtained by integrating

$$\varepsilon_{\text{creep}} = [A_1 t^m] \left[A_2 e^{-\frac{Q_0}{RT}}\right] \left[A_3 \sinh\left(\frac{V_a}{RT\sigma}\right)\right] \tag{3}$$

where V_a is activation volume, activation energy per unit stress. The first term can be determined by a creep-time test, the second by a creep-temperature test, and the third by a relaxation test or other methods.[16]

Klug and Wittmann[15] deduced from their analysis that the creep element must be gel particles. Gamble and Illston[19] and Day and Gamble[20] suggested that, in cement paste, there exist many elements having a wide range of activation energies; hence the hypothesis must invoke an activation spectrum.

Theories that involve water diffusion within cement paste have the difficulty that the pore water cannot transmit a load. A creep theory with load-bearing adsorbed water appeared to overcome this difficulty.[21–25] Powers[21] showed that water in capillary pores can transmit pressures while, at the same time, remain mobile. Powers[26] estimated that interlayer water viscosity is about 50 000 times higher than that of bulk water because interlayer spaces are probably less than four water molecules wide. Peschel[27] showed that the viscosity of water between two plates 8 nm apart is 11 times higher than the viscosity of bulk water.

It was suggested that a state of equilibrium exists between the tensile bonds between particles and adsorbed water compressed in narrow spaces between particles. Creep occurs when additional stress is imposed on these load-bearing layers. This theory explained several experimental results, such as, the lower the moisture content, the lower the steady state creep rate.[9,23–25] However, this idea cannot explain the Pickett effect, the observation that deformation during simultaneous drying and loading is greater than the sum of the two when measured separately.

Bazant addressed the problem of the Pickett effect[28] by introducing multiphase thermodynamics theory.[29–32] But the first intention of the theory was to overcome the difficulty pointed out by Feldman and Sereda[1] that the classical thermodynamics are not applicable to films of water as thin as those present in the areas of small pores. Thus, in the theory, cement paste is treated as a two-phase material in which diffusion of both pore water and solid particles occurs; the movement of solid particles is considered to be the direct source of creep. Based on this analysis, macroscopic constitutive equations for creep and shrinkage have been developed, which are valid whether the evaporable water is capillary, interlayer, or adsorbed. With regard to the Pickett effect, the total diffusion of water is separated into two parts, microdiffusion between adjacent pores in all directions, and macrodiffusion associated with a drying or wetting process at the macrolevel. The microdiffusion makes no contribution to macrolevel drying or wetting, but it makes the solid phase more mobile and therefore increases the potential for creep deformation.

The microdiffusion theory has been developed further using the Kelvin chain model.[10,33,34] The mechanism is called the stress-induced shrinkage for drying creep. The differential equation for a single Maxwell unit is

$$\frac{\dot{\sigma}}{E} + \frac{\sigma}{V_d} = \dot{\epsilon} - \dot{\epsilon}_{sh} \tag{4}$$

where V_d is dashpot viscosity, $\dot{\epsilon}$ and $\dot{\epsilon}_{sh}$ are rates of total strain and shrinkage strain, respectively, E is elastic modulus, and σ is stress. According to Bazant's derivation,[10] $1/V_d$ is a linear function of microdiffusion flux, H_{micro}, and H_{micro} is a linear function of relative humidity and temperature at macrolevel

$$\frac{1}{V_d} = \frac{1}{V'} + k'|H_{\text{micro}}|$$
$$H_{\text{micro}} = a_1\dot{H} - a_2\dot{T} \tag{5}$$

in which V' is viscosity without the effect from microdiffusion, and k', a_1, and a_2 are constants. By combining all three equations, the shrinkage coefficients, k_{ij}, in three dimensions can be determined:

$$k_{ij} = k_{sh}[\delta_{ij} + (r\sigma_{ij} + r'\sigma^{v}\delta_{ij})\text{sign}(H_{\text{micro}})] \tag{6}$$

in which k_{sh}, r, and r' are constants, $\sigma^{v} = \sigma_{kk}/3$, δ_{ij} is Kronecker delta, and sign(H_{micro}) is the sign of H_{micro}. k_{ij} is a function of stress components; that is why the corresponding mechanism is called stress-induced shrinkage. Actually, the stress-induced shrinkage is a combination of seepage theory and viscous shear theory, but is applied at the micro-level. The drying creep is explained by the combination of four phenomena: basic creep, shrinkage, microcracking effect, and stress-induced shrinkage. The existence of stress-induced shrinkage has been demonstrated experimentally by drying a creep test of eccentric loaded prisms.[35] A corresponding theoretical model has also been developed.[36]

Cement paste is a material that ages because hydration continues for long periods. Creep decreases with the age of the material before it is loaded. A model developed to explicitly consider aging is solidification theory.[37,38] Generally, solidification theory considers that material properties develop with age. The cement paste is divided into three parts: a liquid part which cannot bear load, and two solid parts which can bear load, called effective load-bearing parts, one reactive and the other nonreactive. Thus, the total creep is described by two terms, the flow term and the solid term. The key feature of the theory is that the aging aspect of creep of cement paste is due to an increase of the volume fraction $v(t)$, of the effective load-bearing portion of solidified material (i.e., hydrated cement), where t is the age of the cement paste. The properties

of the load-bearing material depend on age. Thus, previously developed models can be applied to the load-bearing material and the aging effect is handled by $\rho(t)$, which can be evaluated by aging tests at the macro level.

Combined Mechanisms

Each of the proposed mechanisms listed above may be considered to be the basis for a mathematical model for creep. A complete description of creep may combine more than one mechanism, such as combining seepage and viscous shear theories[39] or enhanced seepage theory[40] Not all of the mechanisms have been developed rigorously, that is, by mathematical formulation. Of the mechanisms listed above, activation energy, load-bearing adsorbed water, multiphase thermodynamics, stress-induced shrinkage, and solidification theory have been developed to give mathematical relationships. This, however, does not necessarily mean that these models are conceptually more precise, only that the ideas implicit in them have been developed quantitatively. Just as a mathematical model must be physically sound, a conceptual model must be expressed mathematically before it can have widespread usefulness.

Shrinkage

Several terms are necessary to describe shrinkage. *Autogenous shrinkage* is a small shrinkage that occurs during the hydration of a sealed specimen. *Plastic shrinkage* is the deformation of fresh cement paste or concrete. *Carbonation shrinkage* is the result of cement paste reacting with carbon dioxide. *Drying shrinkage* occurs when hardened cement paste dries. Only drying shrinkage is controlled by mechanisms similar to those that control creep; in other words, there is a strong interplay between the quantity of water present, the motion of water, and both creep and shrinkage. Also, the magnitude of creep and shrinkage and their relative reversibility on unloading or rewetting are similar. Here we deal only with drying shrinkage. From the observation of typical bulk shrinkage-weight loss relations (Fig. 2), one can clearly see several discontinuities. This suggests that at different relative humidity ranges there are different dominant mechanisms.

Mechanisms and Models for Shrinkage

Mechanisms for shrinkage have been discussed by several authors.[42–45] Here we will review briefly the proposed mechanisms and discuss some important recent developments.

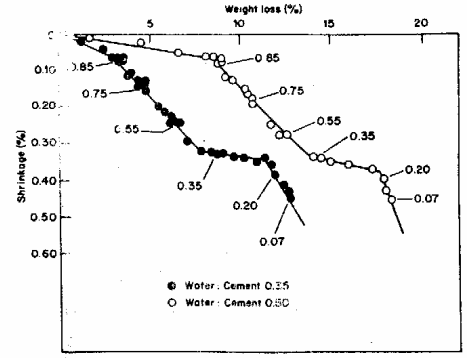

Fig. 2. Typical shrinkage—weight loss curves of portland cement. Reprinted with permission from Ref. 41, The National Research Council.

One mechanism for drying shrinkage is surface tension on the gel particles of cement,[14,46,47] which is a result of the surface free energy. This creates a tensile stress on the surface of the particles and compressive stresses within the solid. This tension is decreased by adsorbed water molecules and, if they are removed, the stress increases and the particle tends to contract. The increment of surface free energy, dF, can be expressed in terms of specific surface area by the Gibbs adsorption equation

$$dF = \frac{0.001RT}{V}\int\frac{V_l}{S}d(H) \tag{7}$$

where V is the molar volume of adsorbed liquid, V_l is the specific volume of adsorbed liquid, and S is the specific surface area of the solid. Thus, the length change of cement paste can be related to the increment of surface free energy by an empirical equation proposed by Bangham.[48]

$$\frac{dl}{l} = A_s(dF) \tag{8}$$

where dl is the length change, l is original length, and A_s is a constant. Surface tension is the dominant mechanism only at low relative humidity, rh < 30%. At high relative humidity levels, the surface will be covered by multilayers of water and the surface tension is not enough to cause the bulk shrinkage.

Capillary tension is a mechanism that may contribute to the total shrinkage at high humidity.[21,49] Water in cement paste forms curved menisci within small capillaries and associated tensile forces are governed by the Kelvin equation. This creates an attractive force, P, between the walls of the pore

$$P = S_w \left(\frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \tag{9}$$

where S_w is surface tension in water, and ρ_1 and ρ_2 are radii of the pore. For a small pore, P is large; for example, in a pore of 2.5 nm diameter and 40% rh, P reaches its maximum value, the tensile strength of water is exceeded, and menisci cannot exist. Thus, capillary tension contributes to shrinkage only at a high humidity level. Hansen[47] has suggested that the shrinkage in addition to that caused by surface tension is induced by capillary tension.

Consideration has been given to disjoining pressure as the cause of shrinkage. Bangham[48] described the dilation of porous solids accompanying adsorption of water molecules as the result of a wedge-like action resulting from molecular bombardment at sharp reentrant angles on the surface. Bangham's wedge-like action led Powers and others[21,50,51] to propose models in which water exerts a swelling or disjoining pressure. Disjoining pressure is the transverse normal stress resulting from water layers on two surfaces of a wedge-shaped structure. Water in such a wedge-shaped structure must maintain equilibrium with the surrounding relative humidity (see Fig. 3). A drop in the external relative humidity and, in turn, the relative humidity in the capillary pores requires water to move from the narrow to the wide side of the wedge in order to maintain equilibrium; thus the water layers become thinner and shrinkage occurs. Disjoining pressure is associated with multilayer adsorption and therefore contributes to shrinkage only at a high relative humidity level. Setzer[52] has tried a method for separating the effects of disjoining pressure from surface tension at a high relative humidity level. Disjoining pressure has been measured by Derjaguin,[53] Wittmann and Splittgerber,[54] and Ferraris and Wittmann.[46] Ferraris and Wittmann considered the extra shrinkage that cannot be explained by surface tension to be induced by the mechanism of disjoining pressure.

Interlayer water has also been considered to be an important mechanism of shrinkage.[1,55,56] C-S-H is assumed to be a layered structure, and the interlayer water is responsible for the major portion of volume change. This mechanism

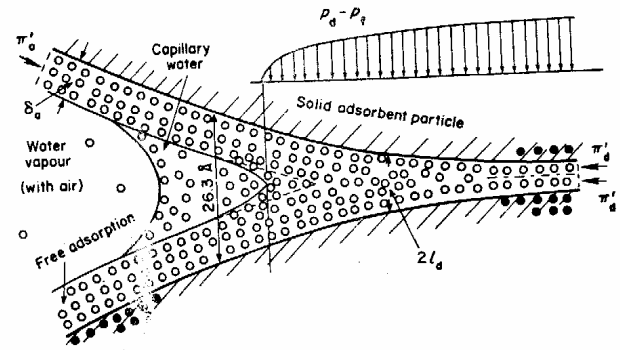

Fig. 3. Schematic representation of disjoining pressure. Reprinted with permission from Ref. 57, Pergamon Press.

is essentially the same as disjoining pressure, but occurs between layers that are much more closely spaced than the pore size. At high relative humidities, the interlayer space is filled by water, so the shrinkage is not significant. It is generally assumed that the large amount of bulk shrinkage at low humidities, say less than 11%, which is the relative humidity at which a monolayer is stable on a free surface, is the result of the loss of interlayer water.

Other mechanisms of shrinkage are:

- Water diffusion that causes dissolution and reprecipitation of certain solid components.[57]
- A stabilization process associated with reduction of surface area and promotion of silicate polymerization.[58]
- Transport of material between the load-bearing and load-free domains.[59,60]

Effect of Microcracking

As discussed previously about the Pickett effect, one much discussed possible reason for enhanced shrinkage under stress is that the true shrinkage of C-S-H is much greater than the measured bulk values because of a compensating "expansion" that reduces the measured value in the absence of applied stress. In

other words, unconstrained shrinkage, which is large, operates under compressive stress. Specifically, compressive stress compensates the internal tensile stress caused by drying, and therefore the compensating effect of microcracking is reduced. Thus, drying shrinkage in the absence of applied compressive stress must have a microcracking component.

Water diffusion is a very slow process, the moisture distribution within specimen generally is not uniform, and the shrinkage distribution is not uniform, which induces stress and causes microcracks. Thus, microcracking is always associated with a diffusion process and, therefore, with a shrinkage process. Microcracking may even occur at high relative humidities as a result of shrinkage stress developed near nonshrinking CH crystals.[61] Microcracks affect the measurement and mechanisms of shrinkage in several respects, including problems of separating deformation due to shrinkage from deformation due to cracking. The latter contributes to irreversible shrinkage and influences diffusivity and permeability. The changes of diffusivity and permeability influence the moisture transport process within cement paste, which further complicates detailed modeling.

Microcracks have a direct effect on shrinkage. Actually, the diffusion process is size-dependent, as shown by the transformation of the diffusion equation into a nondimensional form. The nonlinear diffusion equation for cement paste is

$$\frac{\partial H}{\partial t} = k \operatorname{div}_x(C \operatorname{grad}_x H) \tag{10}$$

where C is diffusivity, k is the inverse slope of the desorption (or adsorption) isotherm, and $1/k$ is called moisture capacity. Both C and k are the function of H, which result in the nonlinearity of the equation. Then, taking

$$\xi = \frac{x}{D}, \qquad \tau = \frac{t - t_0}{\tau_{sh}}, \qquad \tau_{sh} = \frac{a_s}{C_1} D^2 \tag{11}$$

where D is thickness of specimen, t_0 is the starting time of drying, and a_s and C_1 are constants, and substituting Eqs. (11) into Eq. (10) the nondimensional form of the diffusion equation is obtained

$$\frac{\partial H}{\partial \tau} = \frac{a_s}{C_1} k \operatorname{div}_\xi(C \operatorname{grad}_\xi H) \tag{12}$$

The solution of Eq. (12) is independent of size. And with different sizes one can see from Eq. (11) that

$$t = t_0 + \tau \frac{a_s}{C_1} D^2 \tag{13}$$

This shows that according to the diffusion theory the drying time (the time to reach the same τ at the same depth) is proportional to thickness squared.[62] This also means that the extent of microcracking varies with specimen size. This is the main reason that the shrinkage measurements reported in the literature show a large scatter, since up to now no standard specimen size has been adopted. The distributed microcracks reduce the measured shrinkage.

The unperturbed ultimate shrinkage (shrinkage at zero humidity), also called unrestrained ultimate shrinkage and referred to above as true shrinkage, is obtained by reducing the effect of microcracking to the minimum. Very thin specimens have been used. Hwang and Young[63] used specimens with thickness less than 2 mm, and the specimens of Ferraris and Wittmann[46] were 1 mm, Feldman[64] 1.3 mm, Bazant et al.[65] 0.7 mm, Sabri and Illston[66] 0.8 mm, and Hansen[47] 2.3 mm. Because of the size dependence of shrinkage, Klug[67] measured shrinkage of specimens with thicknesses varying between 0.5 and 20 mm, and used the results to extrapolate to zero thickness, in order to predict ultimate shrinkage. Ferraris and Wittmann[46] and Wittmann[68] measured the shrinkage of specimens with different lengths to predict the ultimate shrinkage by extrapolation of the transition from plane strain to plane stress.

Based upon the above consideration, the relationships between unrestrained shrinkage and relative humidity have been predicted from very thin specimens.[46,47,66,69–71] These results have shown that shrinkage keeps a linear relation with humidity in the range 50–100% (commonly used range in practice), within the range of water-to-cement ratios of 0.4–0.6, temperature −5°–+20°C, and age 7–28 days. In the low-humidity range, these quantities vary with relative humidity in a nonlinear manner (see Fig. 4).

On the other hand, observations by light microscopy of the microcracking due to drying have shown that microcracks formed at the beginning of the drying process eventually close.[63] This suggests that shrinkage under near-equilibrium conditions after initial drying does not induce differential stress or constraints. However, from evidence at the macrostructural level, even after crack closure, the residual strain is still very large, sometimes up to several hundreds of microstrain, and cannot be distinguished from micrographs alone. These residual strains affect the measured shrinkage.[10,33,35,36]

Systematic observations by scanning electron microscopy of the samples that have undergone various degrees of drying have revealed very few small cracks in

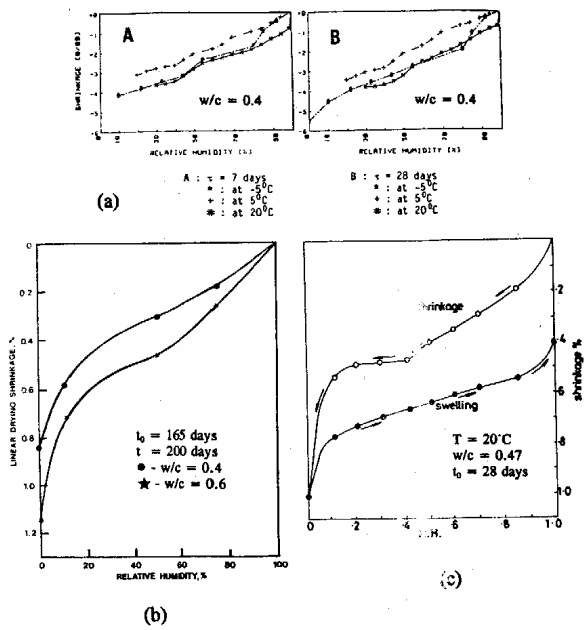

Fig. 4. Shrinkage of hardened cement paste. (*a*) Reprinted with permission from Ref. 46, Pergamon Press. (*b*) Reprinted from Ref. 47. (*c*) Reprinted with permission from Ref. 66, Martinus Nijhoff.

the hydration product.[72] This result must be checked by new techniques that do not require the specimen to be dried completely before observation, such as the environmental scanning electron microscope (ESEM).

Diffusivity and permeability are influenced by microcracking and vice versa. This mutual interrelationship is not usually incorporated into models. Thus, most diffusivity and permeability measurements are complicated by the effects of microcracking. Both theoretical prediction and experimental observation[73,74] show that drying more likely produces discontinuous microcracks than continuous macrocracks, and their width must be of the order of a few micrometers. However, these specimens were observed in the high vacuum of an SEM. By using ESEM and maintaining the specimen at high relative humidities the crack width can be measured more accurately.

Powers et al.[75] have reported experimental results about the effect of drying on permeability of cement paste. They showed that the resistance to water flow through the virgin specimens was 70 times greater than those of companion specimens that underwent a cycle of drying to 79% relative humidity and resaturation. Short circuiting of previously unconnected pores and shortening of the effective water path length are the reasonable explanations,[76,77] however, each of the above alternatives is equivalent to internal microcrack formation.[78]

Bazant and Raftshol[73] obtained relationships between microcrack width and diffusivity and permeability by using fracture mechanics analysis, which show that both diffusivity and permeability are the function of the cube of crack width. Thus, the microcracking induced by nonuniform shrinkage can increase the diffusivity and permeability by several orders of magnitude, which is confirmed by Powers' test results. The effect of cracks on the rate of drying is at first negligible but can increase strongly as the cracks become deeper. The increase is roughly proportional to the square of the depth of penetration of drying.

One topic that must be investigated in the future is the quantitative features of the effect of crack width and, more importantly, the effect of microcrack density on drying and shrinkage. The crack density may be defined as the number of cracks per unit area, the area fraction of the cracks, the perimeter of the cracks, or even combinations of these characteristics.[79] The effect of microcracks is not only important to the research of drying shrinkage but also to the evaluation of strength and elastic modulus, because failure probably starts generally from the cracks induced by the drying process. Another topic is the residual strain after microcracks have closed, which will provide a further basis to predict the effect of microcracking on shrinkage measurements.

Combined Mechanisms

Of the above mechanisms, surface tension, capillary tension, and disjoining pressure have been mathematically formulated. The other mechanisms are still in the stage of conceptual interpretation. As we pointed out for creep, quantitative formulation of a mechanism does not necessarily mean that it is more correct than other mechanisms.

A complete description may incorporate more than one mechanism. Various combinations of mechanisms may be adopted. In a recent publication, for instance, Hansen[47] considered that at a low-humidity range surface tension

is a dominant mechanism, while capillary tension may be a dominant mechanism in the high-humidity range. However, Ferraris and Wittmann[46] considered the disjoining pressure to be the dominant mechanism at high humidity, up to 40%, and below 40% surface tension is dominant. Feldman and Sereda[1] regarded the movement of interlayer water to be important below about 30% humidity. Powers[21] considered disjoining pressure to be the most important effect at all humidities. There has been no general agreement as to the relative importance of these mechanisms. At this stage, it is very difficult to say which is correct and which is wrong because there is no direct physical way to make a judgment. Comparisons of curve fitting of the results of the proposed models with experimental results tell nothing about the correctness of the mechanisms used, since the modern optimization technique can fit two different mathematical models equally well with one set of test data.

Many models are proposed to interpret the irreversible characteristic of shrinkage. The understanding of such a phenomenon will be very helpful to the understanding of shrinkage mechanisms since the most significant microstructural change occurs when the direction of moisture diffusion reverses. The mechanism for this behavior could be the collapse of C-S-H layers,[21,58] a sintering phenomenon linked with particle coarsening and loss of surface area,[80,81] formation of new interlayer spaces associated by breaking and remaking of interparticle bonds,[12] transport of solid material under stress through dissolution and recrystallation,[59,60] or stabilization of the gel structure during the first drying process.[82]

Chatterji[83] explained that, during the first drying process, hydration products will be brought closer together to form a more densely packed arrangement. On subsequent rewetting, however, there is an upper limit to the separation of denser packed particles, that is, twice the thickness of the absorbed water layer at 100% rh, and there is no force to undo the rearrangement that occurred to get denser packing. Microcracking and rearrangement of particles are the two contributory factors to the irreversible shrinkage.

Microstructure

All of the creep and shrinkage models proposed are related to microstructural change during the loading and/or drying process. Thus the microstructure has to be described in detail. The only aspect of microstructure that has been studied thus far is microcracking. However, the microstructure at the nanometer level is at least as important to creep and shrinkage. One of the problems of modeling the microstructure related to creep and shrinkage is that the current experimental techniques cannot provide direct visualization of the detailed structure at the nanometer level. Light microscopy, SEM, and the recently developed ESEM can only resolve at the micrometer level. Average structural information can be obtained by some indirect test methods such as adsorption of nitrogen or water and mercury intrusion porosimetry. Since they give no information as to how the pores are arranged in space, conclusions about the pore structure of cement paste have to be drawn by inference.

Models of Microstructure

The most frequently discussed models for the microstructure of cement paste can be classified into three kinds. The first kind is based on adsorption test results, such as that of Powers, Feldman-Sereda, and the so-called Munich model. The second kind is from phase analysis by X-ray diffraction such as the Taylor model.[84] The third is based on the analysis of hydration process and then simulating the process by computer techniques, such as the Jennings-Johnson model.[85] The first two models are of the molecular structure of C-S-H and the third describes the volume and distribution of the phases that make up the microstructure.

The microstructure of cement contains pores that span a large size range. Colloidal C-S-H gel contains fine porosity. C-S-H fills some of the volume between cement grains, leaving larger capillary pores, the volume of which depends on the original water-to-cement ratio and the degree of reaction. Almost all models for C-S-H are based on some sort of layer structure, although the evidence for this is not strong, and they recognize that water plays a very important role and can affect the structure to a greater extent than can other adsorbates. Controversy has focused on the detailed structure of C-S-H and the states of water. C-S-H is by far the most important phase that influences creep and shrinkage. Therefore, three relevant questions must be answered in any model: What is the structure of C-S-H, how is the structure arranged, and how does water move within and between the basic units of C-S-H?

The Powers model[8,86,87] is supported by water adsorption test data. The model considers that the colloidal particles of C-S-H are made up of two or three layers of thin sheets that are bonded together. Bond forces are mainly surface forces. The water within the particle or between the layers is interlayer water, and the water on the surface of particles is adsorbed water (see Fig. 5). The maximum and minimum average distances between the layers are 3 nm (30 Å) and 0.4 nm (4 Å), which can be obtained by analysis of surface area water adsorption.[88] If the water between the layers is removed, it will not reenter. The irreversible interlayer water loss corresponds to irreversible shrinkage. The size of the interlayer space and the entrance of the wedge-shaped space allow only water molecules to enter, a so-called molecular sieve effect, which explains the difference of specific surface areas measured by nitrogen and water adsorption.

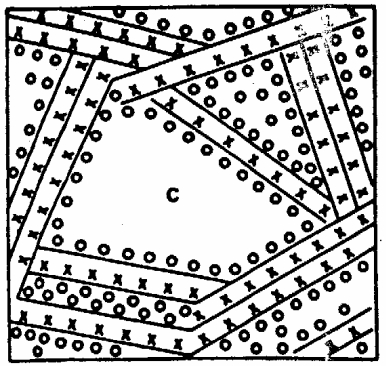

Fig. 5. Powers model for C-S-H. Reprinted with permission from Ref. 43, Prentice-Hall.

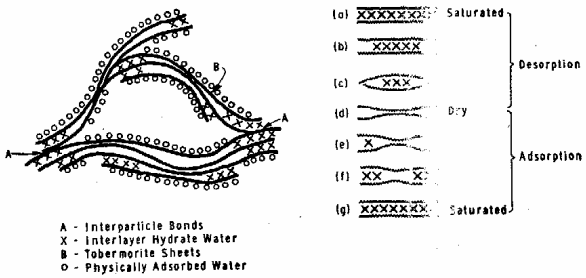

Fig. 6. Feldman-Sereda model for C-S-H. Reprinted with permission from Ref. 1.

Feldman and Sereda[1] suggested that C-S-H is a completely irregular array of single layers (see Fig. 6). Bonding between layers is considered to be through solid-solid contacts. The interlayer water can move reversibly in and out of the interlayer space. Because nitrogen cannot enter the interlayer space, which should not be considered part of the surface, nitrogen adsorption gives a correct measurement of specific surface area. The irreversible deformation comes from the change of interlayer space during interlayer water movement.

Comparing the Powers and Feldman-Sereda models, Young[44] pointed out, "In the light of present-day knowledge, it appears that the differences between the models are due in large measure to the fact that each is referring to different states of C-S-H, and thus emphasize different aspects of the structure." Calculations of bound water indicated that about a third of the gel porosity of the Powers model is interlayer space; the remainder is fine mesopores.[45]

The Munich model[14,89] describes C-S-H as a three-dimensional colloidal xerogel, which is a network of separate colloidal particles as shown in Fig. 7, and no particular internal structure is assumed. The chemical bonds and the van der Waals attraction are equally important in the bonding of the gel particles. The water movement between particles affects surface free energy (low relative humidity level) and disjoining pressure (high relative humidity level).

The Tokyo model[90] is based on water and nitrogen adsorption results. The gel particles are composed of layers and the intragel pores are classified into an intercrystallite type (0.6–1.6 nm) (6–16 Å) and an intracrystallite type (<0.6 nm) (<6 Å) (see Fig. 8). The layer structure inside the gel particle is a combination of the Powers and the Feldman-Sereda models. The intercrystallite pore is similar to the micropore in the Powers model and the intracrystallite pore corresponds to the interlayer space defined in Feldman-Sereda model. The

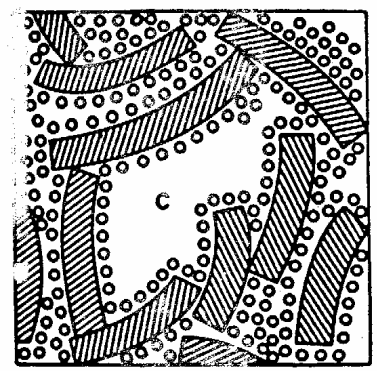

Fig. 7. Munich model for C-S-H. Reprinted with permission from Ref. 43, Prentice-Hall.

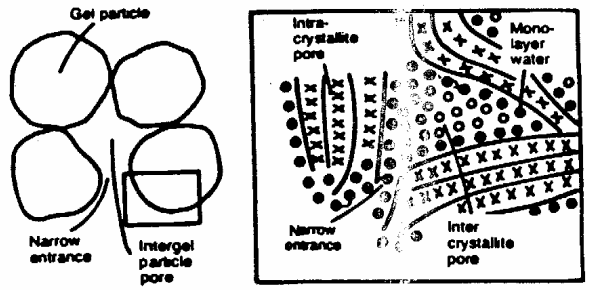

Fig. 8. Tokyo model for C-S-H. Reprinted from Ref. 90.

pores between gel particles are capillary pores (1.6–100 nm) (16–1000 Å). Daimon did not explain the relations of the model with creep and shrinkage mechanism.

Jennings and Tennis[91] have proposed that the basic element, called basic building block, is considered to be a sphere 5 nm in diameter with a specific surface area of 400 m^2/g. The internal structure of the element is layered, of the type proposed by Taylor model. The elements are assembled into one of two types of structure, each with its own structure of specific porosity. Various material properties can be predicted by varying the proportion of each of the three structures formed in the cement paste, which depend on material parameters such as the water-to-cement ratio. The movement of water is reversible but associated changes in structure are irreversible. C-S-H is not considered to be a homogeneous material. Based on recent studies of hydration products by SEM and TEM, the structures of inner and outer products appear to be different. The inner product is a porous, but much more dense structure, while the outer product is composed of similar material but relatively less dense. Based on this consideration, other models may be developed.

There are other models supported by adsorption data: the Chujo-Kondo model[92] and the Hope-Brown model[56] (see Fig. 9).

Taylor has proposed a model[84] at the molecular level. It rationalizes results from thermal graviometric analysis, density, selected area electron diffraction, and analysis of composition by analytical electron microscopy. The proposed

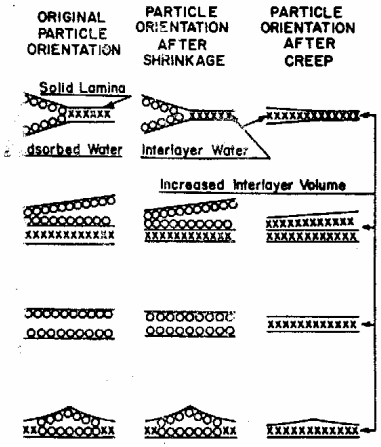

Fig. 9. Hope-Brown model for C-S-H. Reprinted with permission from Ref. 56, Pergamon Press.

structure is an intimate mixture of imperfect jennite and 1.4 nm tobermorite formed into an imperfect array of layers. This structure explains many of the chemical characteristics of C-S-H. Other models of this kind are the Shebl-Helmy model,[93] the Currell model,[94] and the Grudemo model.[95] These models do not explain creep and shrinkage.

Kawamura[96] proposed a mathematical model at the nanometer level that simulates cement hydration as a random clumping process of needlelike gel particles with statistical geometry. The cross section of the needles in this model is shown in Fig. 10. Based on this model, estimates can be made of the average diameters of gel particles, the number of particles per unit volume, and the number of the particles not in contact with others.

The other models of this kind are the Jennings-Johnson model[85,97] and the Cohen-Cohen model.[98] These models are based largely on SEM observations and are, therefore, micrometer-level models.

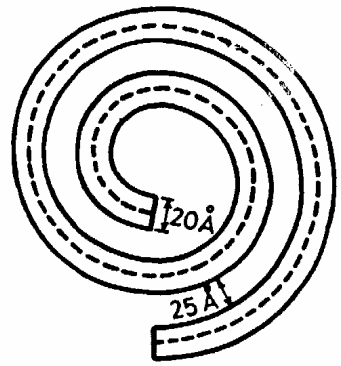

Fig. 10. Cross section of C-S-H needle in Kawamura model. Reprinted with permission from Ref. 96, Pergamon Press.

Relationship of Microstructure Model with Creep and Shrinkage

Background

The mechanisms of creep and shrinkage are associated with changes at the microstructural level, but the models of creep and shrinkage, especially the mathematical formulations, do not have a microstructural interpretation. Perhaps the most important reason for this is the lack of a quantitative description for the microstructure of cement paste. Based on the average information obtained from test results such as the adsorption isotherm, only a few relations between microstructure features and creep and shrinkage have been established.

It is worth recalling the research on the relationships between strength and microstructure at the micrometer level. The volume fraction of pores, or porosity, was the first characteristic of microstructure to be linked to strength. There is evidence, however, showing that strength depends not only on volume fraction but also on the size of the largest pores. Furthermore, the spatial distribution or continuity of the larger pores is a relevant parameter. If, for example, two pores of the same pore size are spaced closely together, the strength will be decreased dramatically compared to the strength of a similar specimen where the pores are dispersed and are not close to one another. However, the spatial distribution is difficult to analyze. Some review articles[99,100] have shown that not much has been done on this topic. Another point is that failure of cement paste is a process that can be described as one with random characteristics and the strength may be defined as the end of the process of random damage accumulation. The starting point of the process likely depends more on cracks than on large pores, because of the special geometry of cracks, that is, a small area with sharp tips. The path of the process depends on the connectivity of large pores as well as the crack distribution.

By analogy to research on strength, the creep and shrinkage behavior have been investigated in the same manner. The first quantity in the nanometer level is surface area. In the mechanism of surface tension, shrinkage has been expressed in terms of surface area. The second quantity is pore-size distribution at the nanometer level, which exerts an influence on the drying shrinkage due to the dependence of capillary stress on pore size, greater capillary stress being induced by the smaller pores. Based on this consideration, Kung[42] related shrinkage with cumulative pore volume. The third quantity is spatial arrangement of pores, which is very important to shrinkage, because the way water goes through the pores affects shrinkage considerably. However, most of the models gave just a schematic figure of the spatial arrangement and, whatever pore structure arrangement is proposed, it is considered to be homogeneous in space. Only the Kawamura model[96] gave a mathematical description of the spatial structure.

Ongoing Research

It is clear from the above review that investigations have concentrated on obtaining qualitative characteristics about the microstructure and relating them to creep and shrinkage mechanisms. However, essentially all of the microstructural features are overall averaged quantities, such as, for example, surface area and pore-size distributions. Further microstructural analysis should focus on the structure of each cement paste component, and then the combined effect may be analyzed by methods for composite materials. In other words, in the same way that concrete commonly is considered to be a composite material, cement paste could also be treated as a composite material with the spatial distribution of C-S-H, CH, the aluminates, anhydrous cement cores, and aggregate considered explicitly. Shrinkage of cement paste is not a homogeneous process, that is, it is not a material property of any single phase, but rather is a process that depends on the distribution of all of the phases present.

Test results have shown that C-S-H particles shrink much more than the measured data from a macroscale specimen. Feldman[101] indicated from his sorption data that the basal spacing of C-S-H crystals varies between 1.24 nm

(12.4 Å) and 0.93 nm (9.3 Å), that is, individually they undergo a volume change of about 30%. Recent observations using the controlled relative humidity in the ESEM to dry C_3S pastes show a shrinkage strain of about 0.02[102] (see Fig. 11, points A and B). This is the first direct measurement of shrinkage at the micrometer level. Since mature C_3S pastes exhibit shrinkage that is approximately 10 times less than these values, only a small volume percent of C-S-H has contributed effectively to the observed dimensional change of the specimen. Similarly, Gutteridge and Parrott[103] showed that for synthetic C-S-H, the interplanar spacing of the (001) planes changed from 1.4 nm (14 Å) to 1.13 nm (11.3 Å) (from saturation to 0.002% relative pressure). The data Odler and Skalny[104] reported are 1.4 nm (14 Å) and 1.16 nm (11.6 Å); the data from Smith et al.[105] are 1.25 nm (12.5 Å) and 0.98 nm (9.8 Å). These data differ from one another due mainly to the different test conditions and experimental techniques used, but they all indicate that shrinkage at the microstructural level never reaches that which is implied at the microstructural level, that is, that major part of the shrinkage of C-S-H has been lost internally. There are, therefore, at least three related problems: restraining effect, microcracking effect, and C-S-H shrinkage.

Fig. 11. Shrinkage of C_3S paste. The measured shrinkage on drying between points A and B is about 0.02. (Courtesy of K. Sujata).

Restraining Effect

Anhydrous grains of cement and CH do not shrink on drying. The spatial distribution of CH crystals and anhydrous cement grains must be analyzed. These might be done by analyzing SEM backscattered electron images, in combination with statistical and autocorrelation analysis. Also, the capillary pores may affect macroshrinkage, because, as a weak zone in the structure of the composite material (cement paste), the pores influence stress distribution and thus the microcracking formation. The distribution of capillary pores must be analyzed explicitly.

Effect of Microcracking

Microcracking in cement paste during drying has been implied by corresponding changes in permeability. However, the direct observation of microcracking is difficult. Ringot,[106] Sicard et al.,[107] and Hwang and Young[63] reported some results about surface microcracking upon drying, but the specimens used were quite thick, and, therefore, the observed microcracking was probably due to differential moisture diffusion, as explained previously. Any microcracking resulting from the restraining stress of CH crystals and/or anhydrous cement grains has not yet been reported. One difficulty with observing this kind of microcracking is that the cracks probably form on an extremely fine scale and, therefore, they are difficult to observe.

Another important aspect of creep and shrinkage is the effect of the rate of drying. This has not been studied on the microstructural level, although macroshrinkage tested at various drying rates has indicated that shrinkage and drying creep are independent of rate of drying.[108,109]

C-S-H Shrinkage

Shrinkage and creep have been modeled primarily through consideration of changes that occur in C-S-H. However, although C-S-H is the most important phase in hardened portland cement paste, other phases, particularly the aluminates, are also present. As shown in Fig. 12, it seems that C_3A particles move randomly. The influence of these phases on shrinkage should be studied explicitly.

At almost every level the microstructure of these materials is heterogeneous. The unreacted cores, CH, C-S-H, AF_t, and AF_m all expand and contract according to individual rules. To make matters even more complex, C-S-H is not, in itself, homogeneous. At least inner and outer products have been shown to be very different in texture and density. These two subphases almost certainly

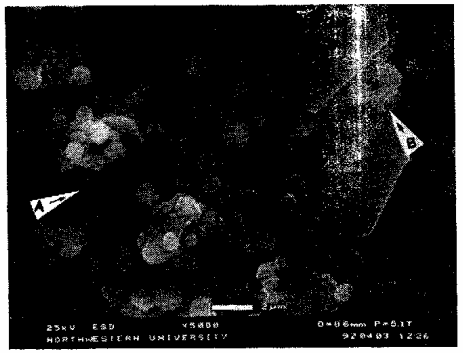

Fig. 12. Shrinkage of C_3A paste. (Courtesy of T.B. Bergstrom).

shrink and expand with the gain and loss of moisture in different ways. Creep and shrinkage will not be understood completely until the behavior of all of the phases and their interaction as a function of their distribution are accounted for explicitly.

Conclusions

Although there are several mechanisms that have been proposed to explain creep and shrinkage, none of these possibilities has been formulated into a theory that is universally accepted. Perhaps the main reason for lack of acceptance is that there is little hard evidence at microstructural level to separate one mechanism from another. In other words, because the various mechanisms can be formulated into mathematical expressions, each of which can fit the data over a limited range, the criterion of mathematical accuracy is not sufficient to establish the correctness of the mechanism. The importance of understanding mechanisms is not only for scientific correctness, but also it is important when extrapolating out of the range for which the mechanisms was formulated. In order to develop a comprehensive theory for creep and shrinkage, it is necessary that the mathematical expressions are compatible with observation at several levels. In particular, it must be physically sensible at the microstructural level, as well as the macrolevel of predicting changes in volume, length, cracking, and other physically observable characteristics of the material.

Acknowledgments

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