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Structure and properties of gels

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Abstract

A brief review is presented of the structure and properties of inorganic gels. The mechanism of formation of gels and precipitates involves the aggregation of polymers or particles. If bonds form irreversibly, fractal aggregates grow and eventually fill space, resulting in a continuous elastic gel network; if the bonding is reversible, then the aggregates reorganize and become more compact, leading to precipitates. The existence of capillary pores in cement paste indicates that C-S-H is a precipitate, rather than a gel. Chemical reactions continue after gelation, leading to increasing rigidity and, in some cases, to spontaneous shrinkage (called syneresis). During drying, capillary pressure on the order of 10 to 100 MPa develops and produces huge shrinkage of compliant gels. As the gel shrinks, its modulus increases by several orders of magnitude; shrinkage stops when the network is stiff enough to resist the capillary forces. For gels, the modulus increases in proportion to the volume fraction of solids to a power between $\sim$3 and 4; consequently, the evolution of the modulus during drying and the final shrinkage can be estimated. Warping and cracking do not depend on the magnitude of the capillary pressure, but only on the gradient in pressure within the body. Slow drying reduces the gradients and prevents damage. The stresses and strains during drying can be calculated in terms of the permeability, physical dimensions, and viscoelastic properties of the gel. A variety of techniques have been developed to measure the latter properties, the simplest of which is a beam-bending measurement. When this method is applied to a rod of cement paste, the permeability and modulus are obtained in a matter of minutes.

Keywords: Drying; Calcium-silicate-hydrate; Aging; Creep; Gel

1. Introduction

Inorganic gels are widely studied for applications in ceramics, including porous membranes [1], sensors [2], thermal insulation [3], dense protective films and passive optical films [4], active optical films [5], and bulk optics [6]. The gels are typically made from molecular precursors, such as metal alkoxides [7] or aqueous salts [8]. In this review we examine features of their structure and properties that these gels have in common with the C-S-H "gel" in cement; in addition, we describe techniques that have been developed for characterization of gels that may be useful for studying cement paste.

2. Sols and gels

Molecular precursors undergo condensation reactions that yield dimers and larger polyatomic clusters (called oligomers) that grow and evolve into particles, precipitates, or gels. If the condensation reaction is irreversible, or if the rate of bond breaking is slow compared to the rate of condensation, then the clusters become fractals [9], as indicated in Fig. 1. A fractal is a structure whose mass increases in proportion to the radial dimension R to a power d_f that is less than 3; since the volume increases as R^3, the density of the fractal decreases as it becomes larger, in proportion to R^{d_f-3}. Consequently, the fractal clusters occupy an increasing fraction of the sol as they become larger, and may eventually fill the space [10]; once they have done so, a continuous network of solid can be formed by developing links between the clusters. The formation of links between the relatively immobile impinging clusters is a process of percolation [11]. At the moment a network forms that extends throughout the volume (i.e., when the clusters percolate), the sol is transformed into an elastic solid called a gel [7]. A gel is a bicontinuous liquid-solid system of colloidal dimensions; that is, one can move from the solid into the liquid, or conversely, without moving as far as a micron. The change in properties (such as viscosity, elasticity, and cluster-size distribution) near the point of gelation obey the predictions of percolation theory [7,12,13].

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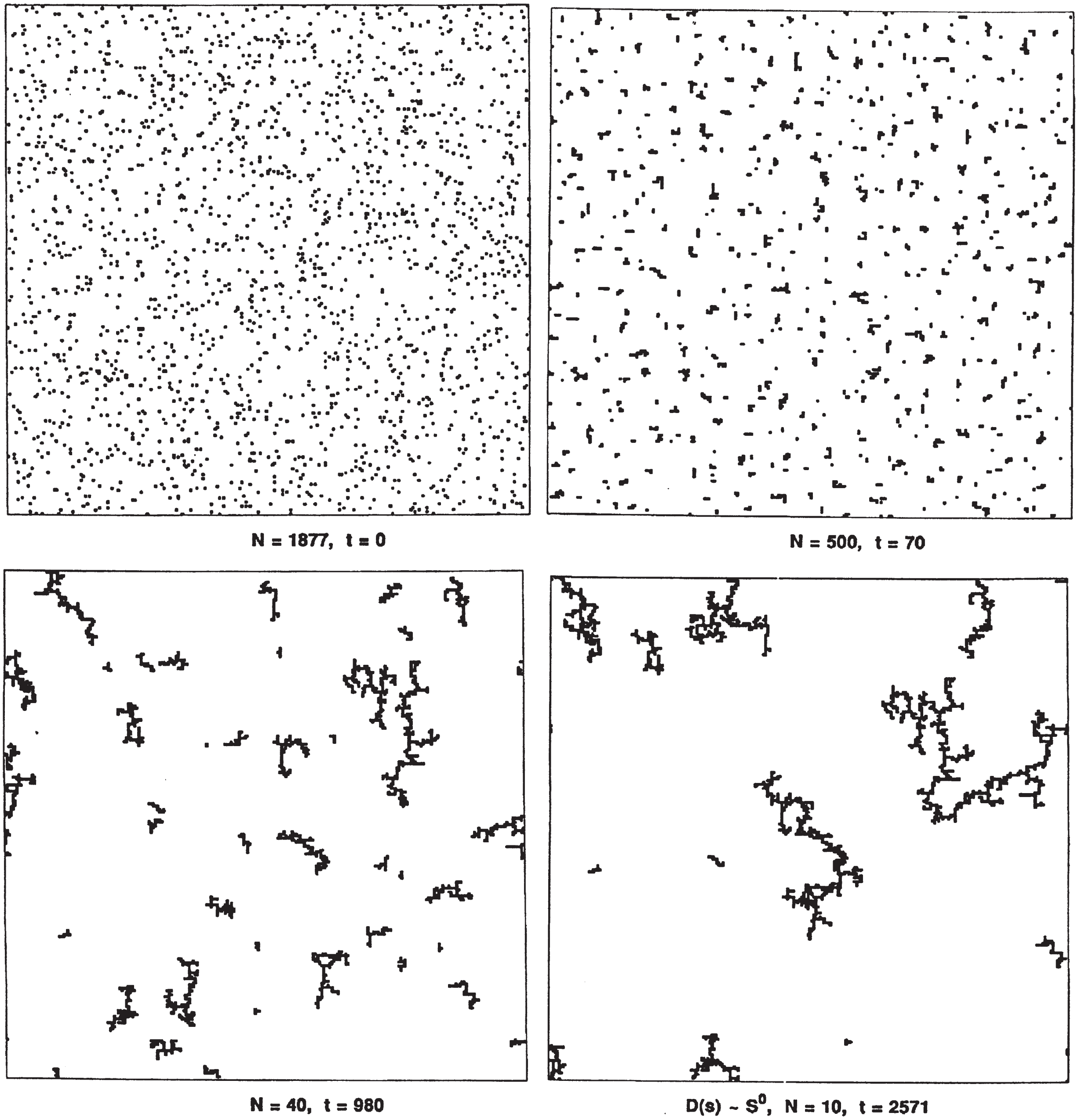

N = 1877, t = 0

N = 500, t = 70

N = 40, t = 980

D(s) ~ S^0, N = 10, t = 2571

Fig. 1. Four stages in computer simulation showing monomers evolving into large fractal clusters by diffusion-limited aggregation. Initial concentration of monomers is 3%. From Meakin [9].

A gel is a structure very far from equilibrium. For example, the equilibrium state of silica under ambient conditions is crystalline quartz, whereas a silica gel is amorphous and has a surface area in the range of 100–1000 m^2/g, which contributes a large additional energy to the material. The energy of the material would decrease by forming more compact structures, such as amorphous particles, and would reduce further by crystallization. The only reason that a structure as energetic as a gel can form is that the bonding reaction is virtually irreversible, so that the approach to equilibrium is kinetically impeded. If the condensation reactions between monomers are reversible, then monomers dangling by one bond will easily detach and reattach, until they are able to make several simultaneous bonds. This process, called “restructuring,” leads to a transport of monomers from the periphery of the cluster toward the center, so that the fractal clusters evolve toward dense particles. Simulations show that a modest amount of restructuring leads to a dramatic change in the density of the clusters that form in solution, as indicated in Fig. 2 [14]. If restructuring is easy, the result of this process is a stable suspension of dense oxide particles; in the case of silica, gels occur at pH below

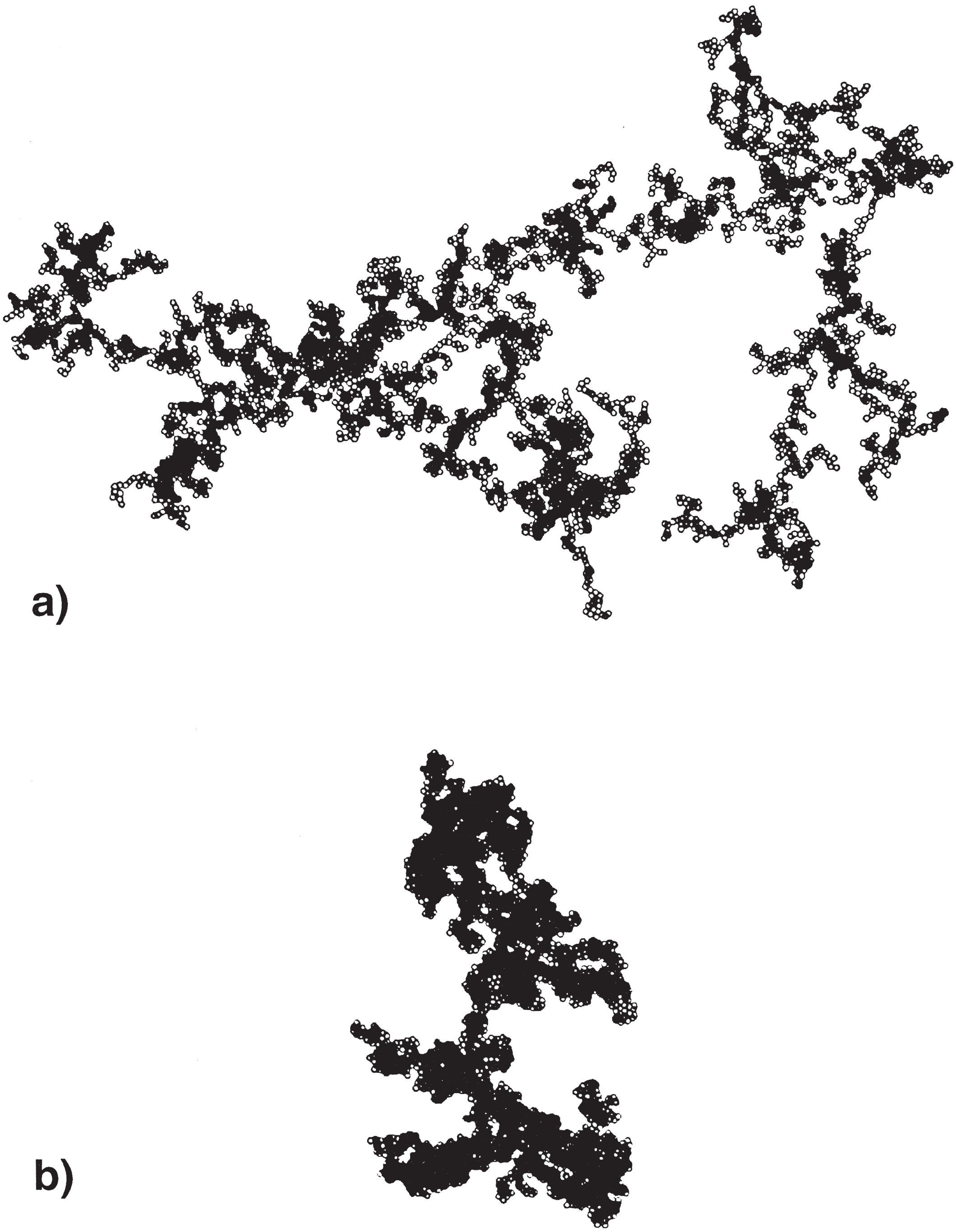

Fig. 2. Clusters of similar sizes grown in computer simulations of diffusion-limited cluster-cluster aggregation allowing (a) no restructuring (as in Fig. 1) or (b) one stage of restructuring. In (b), each particle is allowed to rotate around its point of contact until it touches a second particle. This small degree of restructuring leads to a much denser cluster. From Meakin and Jullien [14]. Reprinted with permission from P. Meakin, R. Jullien, The effects of restructuring on the geometry of clusters formed by diffusion-limited, ballistic, and reaction-limited cluster-cluster aggregation, Journal of Chemical Physics 89 (1), 1988, 246–250. Copyright 1988 American Institute of Physics.

about 8, whereas particles form at pH above about 10 [15], because SiO bonds can be hydrolyzed under those conditions. At higher temperatures and pressures, quartz crystals can form. In intermediate cases, the result is large clusters that are so densely cross-linked that they settle out of suspension; these are called precipitates. These are distinct from gels in that they do not fill space, but the internal structure still consists of continuous liquid and solid materials of colloidal dimensions. The fact that capillary pores (i.e., voids originally occupied by excess water) exist in cement paste means that calcium-silicate-hydrate (C-S-H) does not fill space, so it is a precipitate, rather than a gel.

3. Aging and syneresis

At the point of gelation, the most numerous species in the system is the monomer [7], so condensation reactions continue as oligomers attach to the network, and the elastic modulus increases. The sparse network of the gel contains many flexible branches that can be brought into contact by thermal fluctuations, whereupon new bonds can form. The formation of new links between the branches causes the network to contract and expel liquid in a process called syneresis [16]; this process typically causes linear shrinkage of a few percent over a period of days or weeks. If the pore liquid is capable of attacking the bonds constituting the network, then restructuring will occur by dissolution and reprecipitation of the solid. This reduces the surface area of the network and stiffens the branches, which reduces the rate of syneresis [17] and raises the elastic modulus of the gel [16,18,19]. All of these processes can continue for a period of many months in silica gels under ambient conditions.

4. Gel structure

Inorganic gels made from molecular precursors typically have solids contents below 10 vol%. Measurements on one type of silica gel show that they are fractal on length scales less than ~25 nm for a gel with 5 vol% solids [20]. The very low permeability of gels (discussed below) indicates that the networks are mesoporous, and this is confirmed by transmission electron microscopy performed on supercritically dried gels [21,22]. The transmission electron microscopy images indicate that silica gel networks consist of nodes where three or four chains join; the distance between nodes is several times the thickness of the chains. This makes inorganic gels much stiffer than organic gels, which typically have polymeric coils between the nodes [23]. The elastic behavior of organic gels is controlled by entropic effects and the network is capable of huge changes in volume [24]. In contrast, inorganic gels show very little volume change when exposed to changes in temperature, solvent, voltage, etc.

An important consequence of the high surface area of gels is that a large proportion of the atoms (viz., about half, for a surface area of 500 m^2/g) is exposed at the surface. Reactions at the interface can therefore cause large changes in composition [25].

Single- and multicomponent inorganic gels can be made using virtually every element in the periodic table. In most cases, the gel network is an amorphous hydrous oxide. Some elements, such as Si, Ti, and Zr, readily form three-dimensional networks, but most do not. Many oxides form small particles, which then aggregate into networks; for example, alumina gels typically consist of chains of nanometer-sized particles with a structure close to AlOOH. Tungsten oxide gels have a layered structure with intercalated water [26], so they can absorb and release water as C-S-H does.

5. Drying

The scale of the mesh (i.e., the distance between nodes) in a gel is typically on the order of tens of nanometers, so capillary pressures on the order of 10 to 100 MPa develop when liquid evaporates from the gel; in extreme cases, the tension can be great enough to cause cavitation of the pore liquid [27]. The negative pressure in the liquid creates corresponding compressive stresses in the network, resulting in volumetric contraction by as much as a factor of 10 [28]. The gel becomes increasingly rigid as it shrinks, the elastic modulus rising in proportion to ρ^m, where ρ is the volume fraction of solids and $2.5 \leqslant m \leqslant 4$ [29]. It is therefore possible to predict (within usefully narrow bounds) how the modulus will change during shrinkage. At the same time, the pore size controlling the capillary pressure decreases as the gel shrinks, and several studies have shown that the pore radius changes in proportion to the pore volume [30]. Since the change in capillary pressure and elastic modulus can both be predicted, it is possible to calculate the density at which shrinkage will stop [31,32]; this type of calculation has been performed by Fagerlund for cement [33] (although there is a minor error in his calculation, because he does not take account of the volume fraction of liquid when balancing capillary pressure with the compressive stresses in the solid). Drying shrinkage can be reduced by aging before drying (to increase the rigidity of the network) or by changing the surface tension of the liquid (by solvent exchange or by raising the temperature) [32,34,35]. Unfortunately, it has not been possible to predict the final shrinkage in cases where the gel network is viscoelastic [30].

The tendency of a gel to warp and crack during drying does not depend on the magnitude of the capillary pressure, but only on the existence of a pressure gradient [36]. Since the capillary pressure is responsible for the shrinkage of the gel, if the pressure varies with position, then different parts of the gel will contract at different rates. It is the variation in local shrinkage rates that leads to damage. Liquid moves through the network in response to a pressure gradient ∇p according to Darcy's law [Eq. (1)] [37]:

$$J = -\frac{D}{\eta}\nabla p \tag{1}$$

where J is the flux, η is the viscosity of the liquid, and D is the permeability. Until the end of shrinkage, the liquid/vapor interface remains at the surface of the body [7], so the boundary condition is as shown in Eq. (2).

$$V_E = -\frac{D}{\eta}\nabla p|_{\text{surface}} \tag{2}$$

where V_E is the rate of evaporation. This equation indicates that the higher the evaporation rate, the steeper the pressure gradient inside the gel; moreover, for a given evaporation rate, the lower the permeability, the larger the gradient. A larger gradient causes more differential shrinkage, and that is why fast drying is destructive. If the evaporation rate is slow enough, then the pressure remains uniform and the gel shrinks isotropically. The effect of the pressure gradient on drying stresses and warping for viscous, viscoelastic, and elastic materials has been calculated [36].

For a saturated cylinder of gel with radius R whose network is viscous, the axial stress produced during drying is [36]:

$$\sigma_z = 2G_V\left(\frac{V_E}{R}\right)\left[\frac{\alpha I_0(\alpha r/R)}{I_1(\alpha)} - 2\right] \tag{3}$$

where G_V is the shear viscosity of the network and I_n is a modified Bessel function of the first kind of order n; the parameter α is defined by Eq. (4):

$$\alpha = \sqrt{\frac{\eta R^2}{DH_V}} \tag{4}$$

where $H_V = 2(1 - \nu)\, G_V/(1 - 2\nu)$ is the longitudinal viscosity of the network and ν is Poisson's ratio. When $\alpha \leqslant 1$, Eq. (3) reduces to:

$$\sigma_z \approx \alpha^2 G_V\left(\frac{V_E}{R}\right)\left(\frac{r^2}{R^2} - \frac{1}{2}\right), \ \alpha \leqslant 1 \tag{5}$$

The stress is greatest at the surface ($r = R$), so Eqs. (4) and (5) give the maximum stress as:

$$\sigma_z(R) \approx \left(\frac{1-2\nu}{1-\nu}\right)\left(\frac{\eta R V_E}{4D}\right), \ \alpha \leqslant 1 \tag{6}$$

Later, we will apply this equation to drying of cement. Treating cement as a viscous material is reasonable, since it exhibits linear creep (strain rate proportional to applied at load) at small loads [38].

If the gel is constrained, by attachment to a substrate, for example, then stresses develop in the absence of a pressure gradient [39]. If the substrate does not contract, then the stress in the gel is equal to the capillary pressure [36], which is well in excess of the strength of the network. In view of this situation, one would expect gel films to crack regardless of the drying rate, and that is the case for films thicker than ~1 micron [40,41]. However, in thin films there is not enough mechanical energy released by the extension of a flaw to compensate for the energy of the new crack surface, so they *cannot* crack [42]. Similar considerations apply for concrete, where constraint by aggregate or reinforcement creates stresses in the contracting paste. The tendency of the constrained material to crack depends on the strength of adhesion to the substrate and the capacity of the material to release stress through creep, as well as on the thickness [43,44].

6. Mechanics of gels

Since a gel is a composite consisting of a liquid and a solid, the mechanical response of the gel depends on the properties of both phases and on the interaction between them [45]. In particular, when the gel is subjected to a load a pressure gradient is produced within the network, which causes flow of the liquid; consequently, the gel exhibits a time-dependent response to applied loads (owing to movement of liquid), even when the gel network itself is not viscoelastic. This behavior can be described using a constitutive model developed by Biot [46]; the application of the model to gels has been discussed by Johnson [47,48]. The model has been successfully used to describe the response of inorganic gels to drying [36], mechanical loads [49–51], and changes in temperature [52–54] or pressure [55].

6.1. Temperature changes

The thermal expansion coefficients of ordinary liquids are much greater than those of most solids; for example, the volumetric thermal expansion coefficient of water is about 890 ppm/°C, whereas that of cement is ~30 ppm/°C. Consequently, when the temperature rises, the liquid in a saturated body tends to expand and flow out of the body. However, if the temperature rises fast enough, the liquid does not have time to flow out as it expands, so it expands within the porous body and stretches it. If the temperature stops rising, the liquid will flow until the pressure is zero everywhere, and the solid network will relax to its proper dimension. This phenomenon is readily observed in gels and has been quantified [52,56]. The kinetics of the expansion of a cylinder of gel depend on the characteristic time, τ:

$$\tau = \frac{\eta R^2}{DH} \tag{7}$$

where R is the radius of the cylinder and H is the longitudinal elastic modulus of the network; $H = (1 - \nu)E/[(1 + \nu)(1 - 2\nu)]$, where E is Young's modulus and ν is Poisson's ratio for the drained network. Thus, the gel responds slowly if its permeability is low (because it takes longer for liquid to flow out of the body) or its modulus is low (because the compliant network exerts less pressure on the liquid). Fig. 3 shows the thermal strain in a rod of silica gel subjected to heating and cooling at 0.5°C/min. During heating, the gel expands with an expansion coefficient nearly equal to that of the pore liquid (ethanol) as the network is stretched by expansion of the liquid. During the isothermal hold, the liquid drains out of the gel until the network retracts to its initial dimension (since the thermal expansion of the silica network is negligible over this temperature range). During cooling, the liquid forces the network to contract, but it springs back to its initial dimension during the hold. The dashed and dotted curves in Fig. 3 indicate that the kinetics of expansion are very accurately predicted by the theoretical model [52], where the only free parameter is τ. Similar transient response to changes in temperature is expected to occur in cement and concrete. Measurements reported by Ai and Young [57] on thermal expansion of cement paste appear to show exactly the phenomenon illustrated in Fig. 3.

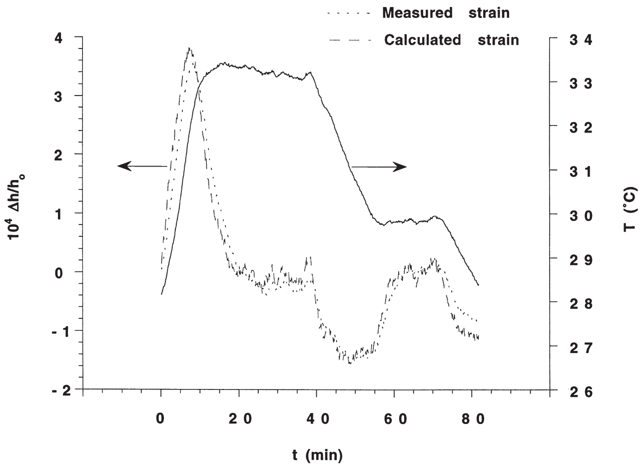

Fig. 3. Thermal strain (dotted curve) of a rod of silica gel subjected to thermal history indicated by solid curve (heating and cooling rate = 0.5°C/min). Dashed curve shows calculated strain, where the only fitting parameter is τ, given by Eq. (7). Data from G.W. Scherer et al. [52].

6.2. Bending

If a rod of gel is bent, a pressure gradient is created within the network; as liquid flows within the gel, the force required to sustain a fixed deflection of the rod decreases with time [49]. As a result of this phenomenon, a simple three-point bending experiment can be used to determine the permeability as well as the elastic modulus of a gel. In the experiment, a rod of gel is supported at the ends while immersed in a bath of liquid, and the rod is suddenly bent by driving a pushrod down against the middle of the gel. After the rod is deflected by the desired amount, the pushrod stops moving, and the force exerted by the gel against the pushrod is measured as a function of time. At the instant that the deflection is produced, the liquid has had no time to flow, so the volume of the gel rod is fixed (due to the virtual incompressibility of the liquid). Since the rod is bent at constant volume, the initial force provides a measure of the shear modulus, *G*, of the gel network. Once the liquid has finished flowing (so that the pressure in the liquid is zero everywhere), the volume of the network relaxes and—as in a conventional three-point bending experiment—the force provides a measure of Young's modulus; given *G* and *E*, we can find Poisson's ratio for the gel. Most importantly, the time required for relaxation of the force depends on the rate of flow of liquid through the network. Therefore, by analyzing the kinetics of the relaxation, it is possible to obtain the permeability of the network. By applying Biot's constitutive equation, the kinetics can be shown to obey Eq. (8):

$$\frac{W(t)}{W(0)} = \frac{2(1+\nu)}{3} + \frac{(1-2\nu)}{3}\sum_{n=1}^{\infty}\frac{8}{B_n^2}\exp\left(-\frac{B_n^2 t}{\tau_b}\right) \tag{8}$$

where $W(t)$ is the force applied at time t, B_n is a root of the Bessel function of the first kind or order 1, $J_1(B_n) = 0$, and the characteristic time is:

$$\tau_b = 2(1-\nu)\frac{\eta R^2}{DH} \tag{9}$$

Thus, by fitting the measured relaxation curve to Eq. (9), one obtains τ_b. Since E and ν are found from the load-displacement values, one can calculate H and then find D from Eq. (9). If the network is viscoelastic, then the relaxation function can also be determined using this experiment [50].

7. Mechanics of cement

A slightly more complicated equation applies when the network is so rigid that the liquid is compressed when the rod is bent (as would be the case for a sample of cement, for example). This problem has recently been solved [58], and the result is:

$$\frac{W(t)}{W(0)} = 1 - A + A\sum_{n=1}^{\infty}\frac{8}{B_n^2}\exp\left(-\frac{B_n^2 t}{\hat{\tau}_b}\right) \tag{10}$$

where

$$A = \left(\frac{1-2\nu}{3}\right)\frac{1-\dfrac{K}{K_s}}{1+(1-\rho)\left(\dfrac{K}{K_L}-\dfrac{K}{K_S}\right)} \tag{11}$$

and

$$\hat{\tau}_b = 2(1-\nu)\left(\frac{\eta R^2}{DH}\right)\left[1-\frac{K}{K_S}+\frac{(1-\rho)G}{(1-2\nu)K_L}+\frac{\rho G}{(1-2\nu)K_S}\right] \tag{12}$$

The bulk modulus of the drained network is $K = E/[3\,(1 - 2\,\nu)]$, and the bulk moduli of the liquid and solid phases are K_L and K_S, respectively. The volume fraction of solids in the body is ρ. When $K << K_L$ and $K << K_S$, then Eq. (10) reduces to Eq. (8). If the solid phase is viscoelastic (i.e., if it exhibits creep), then the rigorous solution is complicated. However, if the viscoelastic relaxation time is much longer than the characteristic time in Eq. (12), then the total response can be approximated as the product of Eq. (10) and the uniaxial stress relaxation function [58]. A similar result was found to apply for less rigid systems [50].

As an illustration of the application of this result, we prepared rods of Type I portland cement with water/cement = 0.6, and cast rods with a diameter of 5 mm and a length of ~11 cm. After 66 h at room temperature, the rod was transferred into a bath of pure water and supported at the ends with a span of 10.0 cm. The rod was then suddenly subjected to a deflection of 0.15 mm (corresponding to an axial strain of 5×10^{-4} and a stress of 2.5 MPa). The stress relaxation data are shown, together with a fit to Eq. (10), in Fig. 4. The dashed curve shows the viscoelastic relaxation function, ψ_{VE}, which is represented by the stretched exponential function as shown in Eq. (13):

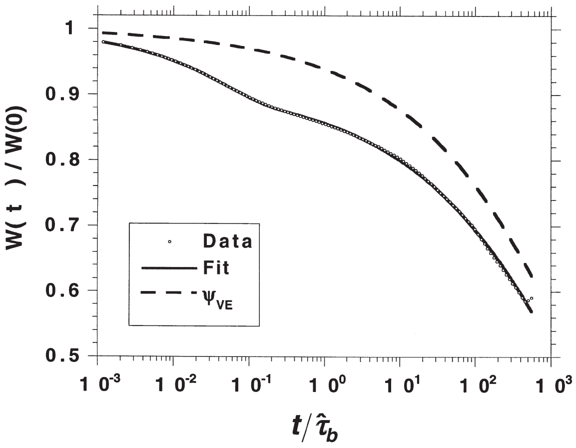

Fig. 4. Load relaxation for a cement rod (water/cement = 0.6, cured 66 h) in pure water. Dots are measured and solid curve is fit to Eq. (10). Dashed curve shows viscoelastic part of relaxation.

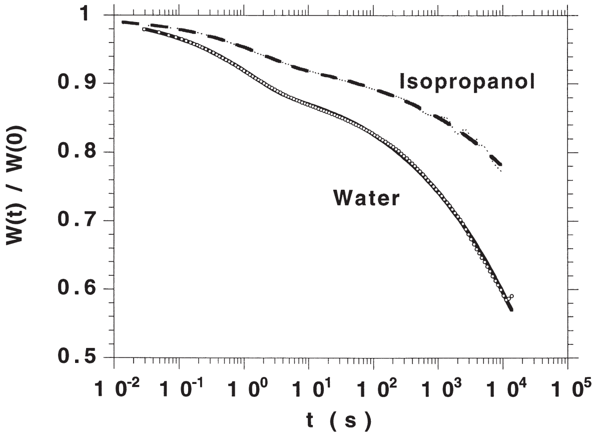

Fig. 5. Comparison of load relaxation for a cement rod (water/cement = 0.6, cured 66 h) in water or isopropanol. Dots are measured and solid curves are fit to Eq. (10).

$$\psi_{VE} = \exp\left[-\left(\frac{t}{\tau_{VE}}\right)^{b}\right] \tag{13}$$

where τ_{VE} is the viscoelastic relaxation time and b is a constant. The fit in Fig. 4 is excellent, and the parameters are reasonable: $\hat{\tau}_b = 24.5$ s, $E = 5.3$ GPa, $\nu = 0.23$, $D = 0.2$ nm^2 (equivalent to 2×10^{-12} m/s), $K_S = 36.6$ GPa. The relaxation parameters were $\tau_{VE} = 1.4 \times 10^5$ s and $b = 0.32$. The same sample was soaked in isopropanol overnight and remeasured, with the results shown in Fig. 5. The main difference is that the creep is much slower when water is replaced by isopropanol ($\tau_{VE} = 1.1 \times 10^8$ s and $b = 0.26$).

These results indicate that the same method that has been used to characterize the permeability and viscoelastic properties of gels can be applied to cement (and probably to mortars, as well). The bending method is simple and avoids the problems of leakage and high pressure that complicate conventional permeability measurements.

Eq. (12) shows that the characteristic time increases with radius squared, so, for the cement used in our experiments, a cylinder 15 cm in diameter would have $\hat{\tau}_b \approx 6$ h. Therefore, one would expect a transient response to temperature changes occurring at a few degrees per hour.

The average viscoelastic relaxation time is related to τ_{VE} by the reaction shown in Eq. (14) [50,59]:

$$\bar{\tau}_{VE} \equiv \frac{3G_V}{E} = \frac{\tau_{VE}}{b}\Gamma\left(\frac{1}{b}\right) \tag{14}$$

where Γ is the gamma function. From the data provided above, we find $G_V \approx 2.3 \times 10^{15}$ Pa • s for our cement, so Eq. (4) reduces to $\alpha \approx 1.4\,R$, where R is in meters. For a cylinder 15 cm in diameter, α is small enough that Eq. (6) applies; the maximum axial stress in a 15 cm cylinder is then that shown in Eq. (15):

$$\sigma_z(\mathrm{MPa}) \approx 6 \times 10^{5} V_E(\mathrm{m/s}) \tag{15}$$

To keep the tension from drying stresses below 3 MPa, the evaporation rate would have to be $V_E < 0.18$ mm/h = 4.5 mm/day. This is a reasonable estimate, considering that the analysis does not take account of the change in properties with time, nor dilatation caused by other chemical processes (such as hydration and carbonation).

8. Conclusions

In a gelling solution, clusters grow with such a low fractal dimension that they eventually fill space; then the formation of a relatively small number of new bonds between clusters transforms the sol into an elastic gel. If the condensation reactions are reversible, then the fractal dimension of the clusters increases, and the resulting denser structures tend to form gelatinous precipitates or particles. The "gel" in cement does not fill space (as indicated by the existence of capillary pores), so it is more appropriate to call it a precipitate. The fact that some crystalline order is found in the C-S-H gel is direct evidence of the reversibility of the condensation reactions (which is to be expected in the aggressive chemical environment of the paste), so it is not surprising that C-S-H does not form a true gel.

Since gelation occurs by linking the larger clusters, the process is described by percolation theory. This means that the change in properties, such as elastic modulus, varies in a predictable fashion near the gel point. The setting of cement paste, which results from precipitation of C-S-H "links" between cement particles, is a similar process. The chemical reactions that bring about gelation do not stop at the gel point, so the properties of gels change over long periods of aging, just as cement paste evolves during curing.

Drying of a gel (or paste) causes shrinkage, because the negative capillary pressure creates balancing compressive stresses in the network. If the effect of shrinkage on modulus and pore size is predictable, then the final drying shrinkage can be predicted. An important effect of aging is that the network becomes more rigid, so that it shrinks less during drying. The tendency of a body to warp or crack during drying does not depend on the capillary pressure; damage results only from a gradient in the pressure that causes differential shrinkage. The magnitude of the gradient depends on the permeability, modulus, and size of the material, and on the rate of evaporation.

The local structure of a precipitate is not very different from that of a gel: a continuous solid network is immersed in a continuous liquid phase, both having colloidal dimensions. Therefore, one can expect that the mechanical behavior of C-S-H will show similarities to that of an inorganic gel, such as silica gel. In particular, the response to applied loads or changes in temperature shows time dependence, because pressure gradients are created in the liquid, and the resulting flow causes transient stress-strain behavior. This time dependence exists even when the solid phase is purely elastic; it is a hydrodynamic relaxation caused by the change in the pressure in the pores. A simple illustration of this effect is the load relaxation of a saturated sample in a three-point bending experiment: the force required to sustain a fixed deflection decreases with time as the liquid flows within the body. This phenomenon can be exploited to provide a measure of the permeability, as well as the viscoelastic properties of a gel, or of cement paste.

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