Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1613–1624

CEMENT AND CONCRETE RESEARCH

Stress from crystallization of salt

George W. Scherer*

Department of Civil and Env. Eng., Eng. Quad. E-319, Princeton University, Princeton, NJ 08544, USA

Received 22 October 2003; accepted 22 December 2003

Abstract

The thermodynamic and kinetic factors influencing crystallization pressure are reviewed for cases including capillary rise and evaporation, cyclic wetting and drying, and hydration of cement. Under equilibrium conditions, where the crystal is surrounded by a film of solution, high stresses are expected only in small pores, but when that film is discontinuous (as may occur during drying), high stresses can arise even in large pores. High crystallization pressure requires a substantial supersaturation of the pore liquid. In the case of sodium sulfate, supersaturation results from the difference in solubility between the anhydrate and decahydrate phases; for ettringite, supersaturation may develop following the cooling from elevated temperatures. During the hydration of Portland cement, crystallization pressure may result from the growth of ettringite and/or calcium hydroxide.

Keywords: Crystallization pressure; Supersaturation; Sodium sulfate; Ettringite

1. Introduction

Porous materials, including stone, mortar, and concrete, can be damaged when crystals precipitate from the liquid in their pores. Salts may be inherent to the material (as is the case in cementitious materials), or be absorbed with ground water or formed by reaction with atmospheric pollutants (particularly sulfates), or created by the metabolic activity of microbes. Whether crystals form, and how much damage they do, depends on the supersaturation of the salt, the size of the pores, and the magnitude of the repulsive force between the salt and the confining pore surfaces. A variety of factors influence the supersaturation, including the nature of the salt (which affects the ease of nucleation) and the rates of the supply of the solution, and evaporation of water. In this paper, we will examine four cases of crystallization pressure: (1) capillary rise and evaporation; (2) cyclic wetting and drying; (3) precipitation of ettringite; and (4) hydration of cement. In each case, we will examine the thermodynamic factors that set bounds on the possible stresses resulting from crystal growth and discuss the kinetic factors that affect stress development.

2. Capillary rise and evaporation

When a porous material, such as stone or masonry, is in contact with the soil, ground water may be drawn into the pores by capillary suction. This is particularly deleterious for walls adjacent to sidewalks exposed to deicing salts [1]. Water may also enter a wall from a leaky roof or water pipes, or from the breath of the inhabitants [2], and mobilize the salts already present in the wall. The capillary rise of ground water is shown schematically in Fig. 1. Water is drawn up into the wall by capillary pressure, p_c (<0), which depends on the pore size distribution and wetting behavior of the porous body. The flux, J, into the wall is given by Darcy's law [3]:

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

where k is the permeability, η is the viscosity, and p is the pressure. If the liquid has risen to height h, then, the pressure gradient is approximately $(p_c + \rho_L g h)/h$, where ρ_L is the density of the liquid and g is the gravitational acceleration. The flux from the capillary rise, J_C, is therefore

$$J_C = \phi A \frac{dh}{dt} = \frac{k}{\eta}\frac{(-p_c - \rho_L g h)}{h} \tag{2}$$

where A is the area of the surface in contact with the ground and ϕ is the porosity of the material. Eq. (2) does not apply

---

* Tel.: +1-609-258-5680; fax: +1-609-258-1563.

E-mail address: scherer@princeton.edu (G.W. Scherer).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.12.034

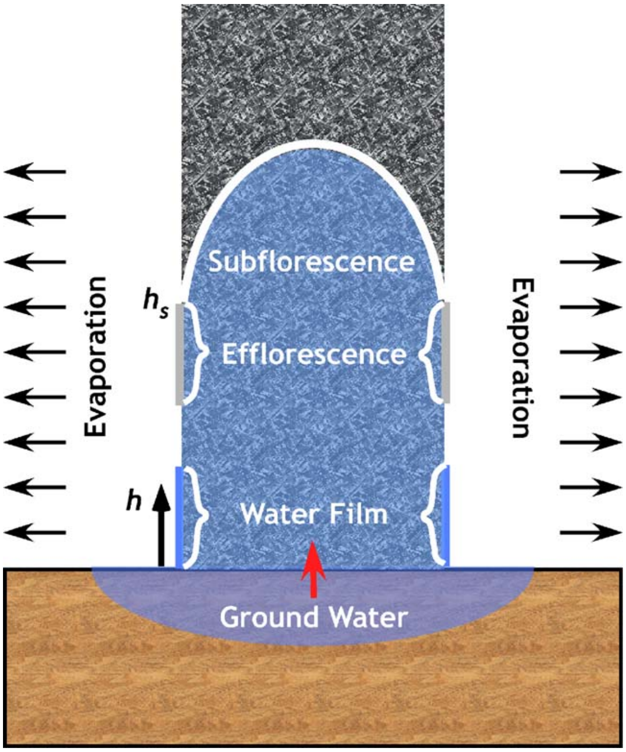

Fig. 1. Schematic of capillary rise and evaporation from a wall in contact with damp soil. Groundwater rises into the wall at a rate that decreases with height, while evaporation from the surface occurs at a nearly uniform rate. Near the ground, where the rate of rise is fast compared with the rate of evaporation, there is a liquid film on the surface of the wall. Evaporation raises the salt concentration in the water, but the diffusion of salt back toward the source may prevent the solution from becoming supersaturated. Higher up the wall, where the rate of rise is slower, the solution may become supersaturated, so that crystals effloresce (i.e., grow in the external water film). At h_s, the rate of supply of water by capillary rise becomes equal to the rate of evaporation; above that location, the water evaporates inside the wall, resulting in subflorescence (i.e., growth of crystals below the surface).

when $t = 0$, where inertial effects are important [4] but is valid at small distances above the ground. Eq. (2) shows that the rate of rise decreases as h increases, whereas the rate of evaporation, J_E, is roughly constant. If the conditions are constant, a steady state will arise where the pore pressure varies linearly from $p = 0$, at ground level, to $p_c + \rho_L g h_s$ at height h_s (see Fig. 1), where $J_C \approx J_E$; if $J_E = 0$, then, h_s is simply the equilibrium height of capillary rise, h_{eqm}:

$$h_{eqm} = -\frac{p_c}{\rho_L g} \tag{3}$$

For example, if water is rising in a material with a mean pore radius $r_p = 0.5$ μm, then, $p_c \approx 2\gamma/r_p \approx 0.28$ MPa, given that its surface tension is $\gamma \approx 0.072$ J/m^2; without evaporation, the water would rise to a maximum height of $h_{eqm} = 29$ m. Suppose that the rate of evaporation is sufficient to volatilize 2 mm of water in 24 h ($J_E = 2.3 \times 10^{-8}$ m/s, as observed in my kitchen at relative humidity $60 \pm 2\%$), then, solving Eq. (2) for $h = h_s$, we find that the water (given $\rho_L = 1000$ kg/m^3, $\eta = 0.001$ Pa s) only reaches a height of about 13 m before the rate of evaporation exceeds the rate of capillary rise. The difference increases as the pore size decreases: if $r_p = 50$ nm, then, $h_{eqm} = 290$ m, but $h_s = 2.3$ m. Near the ground, the pore liquid is near the atmospheric pressure, hence, the menisci in the pore mouths are nearly flat, and a liquid film forms on the external surface of the body. At height h_s, the pore pressure is p_c, and the radius of curvature of the liquid/vapor interface approaches $-r_p$. Above that level, the interface retreats inside the body, and the rate of evaporation decreases, thus, the liquid rises higher inside the wall than at the surface, as indicated in Fig. 1.

When the ground water contains dissolved salts, the situation is a bit more complicated. As water evaporates, the concentration of salt in the liquid near the drying surface rises, and the gradient in the concentration causes the salt to diffuse back toward the source [5,6]. However, as the solute builds up, the diffusive flux away from the surface slows down because the gradient flattens out (that is, the distance to a source of dilute solution increases). Near the ground, where the reservoir of groundwater constitutes a large sink for solute, the breadth of the gradient is limited by the

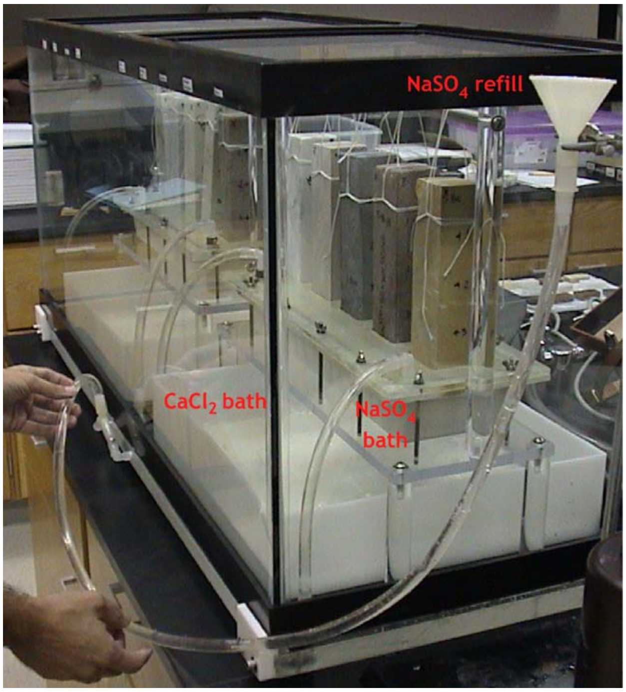

Fig. 2. Salt crystallization is demonstrated in this apparatus, in which samples of stone (5 × 5 × 25 cm) are suspended from a horizontal rod, such that approximately 2 cm of the bottom of the sample is immersed in a solution containing 16 wt.% sodium sulfate. The system is covered with a glass container, and the relative humidity inside the enclosure is controlled at approximately 39% by a saturated solution of calcium chloride. In this case, 10 different types of stone are tested.

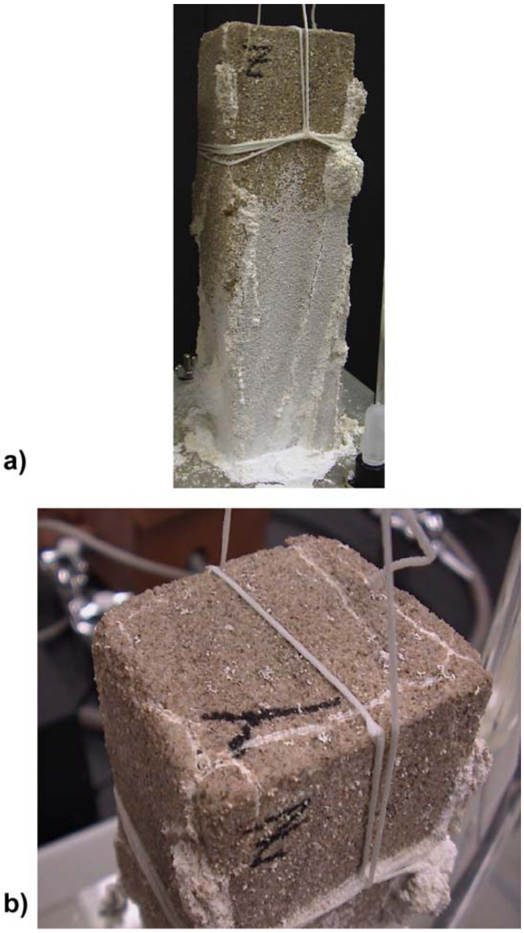

Fig. 3. After 47 days of exposure in the apparatus shown in Fig. 2, this sample of relatively porous Ohio Masillian sandstone shows efflorescence, but little damage, on the bottom half (a). However, the top of the sample is cracked (b), owing to subflorescence of sodium sulfate.

distance to the ground, and the concentration may not reach saturation. Farther up the wall, however, the salt concentration at the drying surface continually increases until the supersaturation is high enough to cause a precipitation of salt. Thus, it is typical [7] to find a zone near the ground that is wet but contains no crystals, followed by a higher zone with efflorescence (i.e., crystals growing in a superficial layer of water). If the crystals grow while submerged in a free film, they grow polyhedral (equilibrium) shapes; where the wall is drier, whiskers tend to form, as ions are only added to the base of the crystal as it grows away from the surface. Crystals of any salt, regardless of their equilibrium morphology, will grow as needles from a porous substrate [8]. At higher levels, there is subflorescence (i.e., crystallization below the surface), and it is in this region that damage may occur if the crystallization pressure exceeds the tensile strength of the porous material.

Damage from salt precipitation during capillary rise is demonstrated using the apparatus shown in Fig. 2, based on the design of Lewin [9]. Prismatic samples of stone are suspended, with the bottom touching a solution of sodium sulfate, which rises into the stone. The relative humidity is kept near 39% by a bath of calcium chloride, so the water evaporates from the stone and the salt precipitates. For

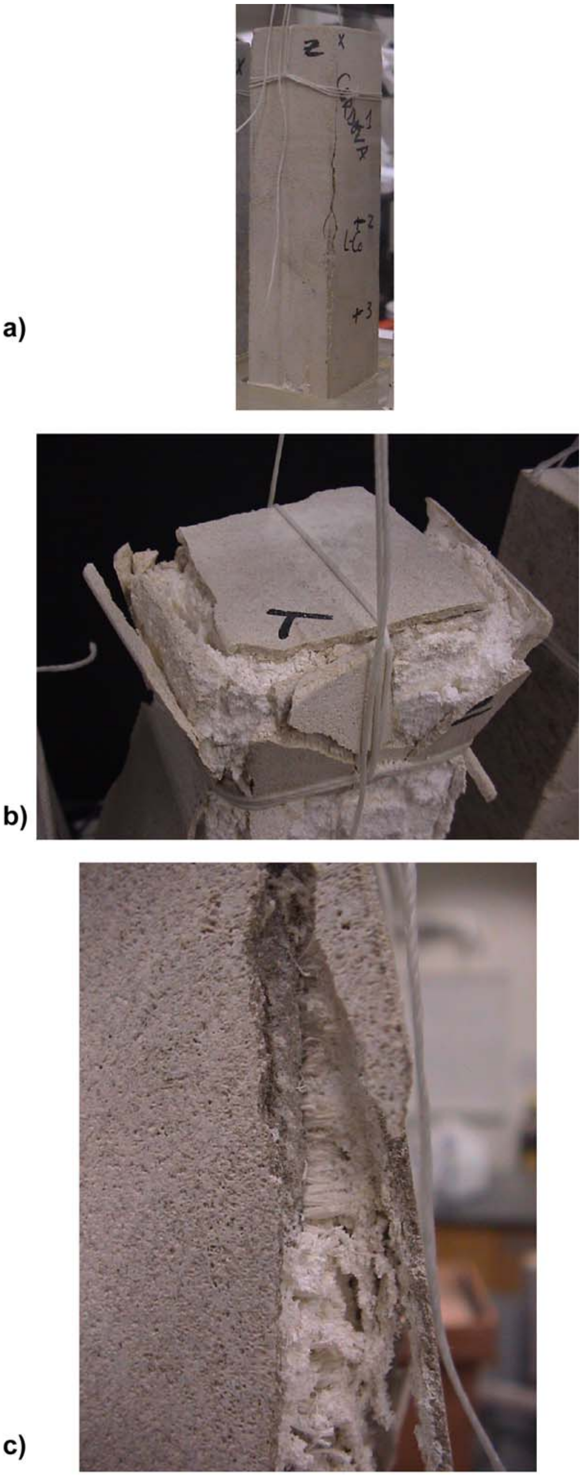

Fig. 4. Sample of Cordoba Cream limestone exposed in the apparatus shown in Fig. 2. (a) After 8 days, there is no sign of efflorescence, but the sample has begun to crack. (b) After 47 days, a layer of stone has separated from all over the surface. (c) A closer view of the sample in Panel (b) shows columnar crystals of salt growing from the surface under the separated layer of stone.

such short samples, the gravitational term in Eq. (2) is negligible, so the height of rise is found to be

$$h = S\sqrt{t} \tag{4}$$

where the sorptivity, S, is

$$S = \sqrt{\frac{2kp_{\mathrm{c}}}{\eta}} \tag{5}$$

The permeability is roughly proportional to the square of the pore size, $k \propto r_{\mathrm{p}}^2$, and the capillary pressure is $p_{\mathrm{c}} \propto 1/r_{\mathrm{p}}$, and thus, Eq. (5) indicates that $S \propto r_{\mathrm{p}}^{1/2}$. Fig. 3 shows the result for a sandstone that is relatively porous ($\phi = 0.21$) and permeable ($S = 0.18$ cm/s$^{1/2}$). The bottom half is covered with a layer of efflorescence, but the major damage occurs above that level, owing to the subflorescence of the salt inside the pores. Fig. 4 shows a limestone that is equally porous ($\phi = 0.21$) but less permeable ($S = 0.06$ cm/s$^{1/2}$) than the sandstone. It shows no efflorescence because the evaporation occurs inside the stone, even near the bottom. The difference in the sorptivity of the two stones implies that the pores in the limestone are an order of magnitude smaller than those in the sandstone. Cracks appear on the surface of the limestone after 8 days (Fig. 4a); after 47 days, a layer approximately 2 mm thick has separated from the surface of the entire block (Fig. 4b), and columnar crystals of salt are growing from the newly formed surface (Fig. 4c). This sequence of events is typical of what is seen in the field [7].

3. Crystallization pressure

The tensile strength of the limestone in Fig. 4, as measured by the Brazil test [10], is about 3.8 MPa; thus, the salt growing in the pores of the stone evidently generated stress of that magnitude. The origin of this stress has been analyzed in detail previously, for both equilibrium [11] and nonequilibrium [12] conditions. Suppose that a spherical crystal with radius r is growing in a supersaturated solution, if the crystal/liquid interfacial free energy is γ_{CL}, then, the increase in surface energy resulting from growth is $\gamma_{\mathrm{CL}}\mathrm{d}A$, where $A = 4\pi r^2$ is the surface area. This increase in energy inhibits the growth of the crystal; it is equivalent to applying a mechanical pressure, p, so that the crystal has to do work $p\mathrm{d}V$ as it increases in volume. (For example, imagine that the crystal is surrounded by a semipermeable elastic membrane that allows molecules to move from the liquid to the solid, but not the reverse. As the crystal grows, it must stretch the membrane so that the energy of the crystal is elevated by the amount of mechanical work it must do. The surface energy acts like such a membrane.) Setting the two energies equal, we find the pressure that would have to be imposed on the crystal to raise its energy by the same amount as the surface energy; for a spherical crystal with volume $V = 4\pi r^3/3$, the result is

$$p = \gamma_{\mathrm{CL}}\frac{\mathrm{d}A}{\mathrm{d}V} = \frac{2\gamma_{\mathrm{CL}}}{r} \tag{6}$$

(This is not the Laplace pressure inside the crystal; that pressure depends on the surface stress, rather than the surface free energy, and the two are not equal for solids [13]. The Laplace pressure is related to the work that would have to be done to stretch the surface area, whereas we are increasing the area by adding a material to the crystal without changing the state of strain of the surface.) Eq. (6) indicates the amount of pressure that would have to be imposed to inhibit growth as much as the surface energy does. Since p depends on the curvature of the crystal, which is $\kappa_{\mathrm{CL}} = \mathrm{d}A/\mathrm{d}V$, it has a large effect on small bodies such as the crystals that grow in small pores.

The surface free energy raises the solubility of the crystal so that a small crystal is in equilibrium with a higher concentration of salt than a macroscopic crystal. The solubility product, Q, in equilibrium with a crystal having curvature κ_{CL} is [13,14]

$$\gamma_{\mathrm{CL}}\kappa_{\mathrm{CL}} = \frac{R_{\mathrm{g}}T}{V_{\mathrm{C}}}\ln\left(\frac{Q}{K}\right) \tag{7}$$

where K is the equilibrium solubility for a macroscopic crystal, R_{g} is the gas constant, T is the absolute temperature, and V_{C} is the molar volume of the crystal. The physical interpretation of this equation is that an atom on the surface of a small crystal is in a highly energetic condition; therefore, it has a stronger tendency to hop into the liquid than does an atom on the surface of a large flat crystal. Consequently, to sustain equilibrium, a higher concentration of ions in the adjacent solution is required, so that there is a correspondingly high frequency of atoms hopping from the liquid onto the solid. Eq. (6) indicates that the energy of the small crystal is equivalent to that of a crystal subjected to pressure $p = \gamma_{\mathrm{CL}}\kappa_{\mathrm{CL}}$; inserting this result into Eq. (7), we obtain the result known as Correns' equation [15]:

$$p = \frac{R_{\mathrm{g}}T}{V_{\mathrm{C}}}\ln\left(\frac{Q}{K}\right) \tag{8}$$

This equation indicates that a mechanical pressure applied directly to a crystal raises its solubility. For a crystal growing in a pore, it is the pore wall that applies stress to arrest growth.

Now, consider the case of a crystal growing in a cylindrical pore under conditions of subflorescence, as shown in Fig. 5a. The hemispherical end of the crystal has curvature $\kappa_{\mathrm{CL}}^{\mathrm{E}} = 2/(r_{\mathrm{p}} - \delta)$, where δ is the thickness of the film of solution lying between the crystal and the pore wall [11,12]. The existence of this film is inferred from the fact that a crystal subjected to a load continues to grow,

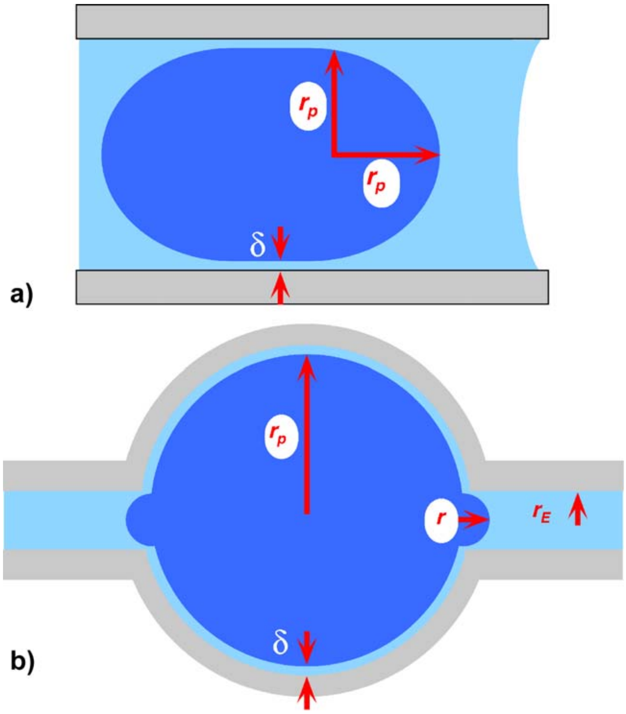

Fig. 5. A crystal has precipitated in a pore with radius r_p in the zone of subflorescence shown in Fig. 1. (a) If the pore is cylindrical, then the end of the crystal is hemispherical and has curvature $\kappa_{CL}^{E} = 2/(r_p - \delta)$, while the cylindrical side has curvature $\kappa_{CL}^{S} = 1/(r_p - \delta)$; here, δ is the thickness of the liquid film between the crystal and the pore wall. (b) When a crystal grows in a large pore (r_p macroscopic) with small entries (radius $r_E \ll r_p$), the curvature of the body of the crystal is $\kappa_{CL}^{S} \approx 0$, and the crystallization pressure is determined by the curvature of the crystal in the pore entries, $\kappa_{CL}^{E} = 2/(r_E - \delta)$.

adding material in the region between the surface of the crystal and the confining surfaces [16–18]. Evidently, there is a repulsive force between the growing crystal and the opposing surface. For ice crystals, the van der Waals forces are repulsive, and the force that would be required to push an ice crystal into contact with a mineral surface is estimated to be tens of megapascals [11]. For salt crystals, the repulsion (or disjoining force) probably arises from a combination of electrostatic and solvation forces. The thickness of the film is estimated to be 1 or 2 nm [12].

If the crystal in Fig. 5a is in equilibrium, then, the solubility product, Q^{E}, of the solution adjacent to the crystal must satisfy

$$\frac{2\gamma_{CL}}{r_p - \delta} = \frac{R_g T}{V_C} \ln\left(\frac{Q^{E}}{K}\right) \tag{9}$$

If the pore is cylindrical, then, the curvature of the side of the crystal is $\kappa_{CL}^{S} = 1/(r_p - \delta)$, so that region of the crystal would be in equilibrium with a lower solubility product, Q^{S}:

$$\frac{\gamma_{CL}}{r_p - \delta} = \frac{R_g T}{V_C} \ln\left(\frac{Q^{S}}{K}\right) \tag{10}$$

Since the liquid surrounds the crystal, the cylindrical side is actually in contact with a solution having the solubility product Q^{E}; thus, it is subjected to a supersaturation whose magnitude is Q^{E}/Q^{S}, and the crystal tends to grow radially. The pressure that would have to be applied to stop its growth is found from Eq. (8):

$$p = \frac{R_g T}{V_C} \ln\left(\frac{Q^{E}}{Q^{S}}\right) = \frac{\gamma_{CL}}{r_p - \delta} \tag{11}$$

where the second equality follows from Eqs. (9) and (10). The pore wall blocks the growth of the crystal and, to do so, it must apply the pressure given by Eq. (11).

More generally, if the most strongly curved part of the crystal, with curvature κ_{CL}^{E}, is in equilibrium with the surrounding solution, then, any other part of the crystal whose curvature is κ_{CL}^{S} must be subject to a pressure from the pore wall, p_w, given by

$$p_w = \kappa_{CL}^{E} - \kappa_{CL}^{S} = \frac{R_g T}{V_C} \ln\left(\frac{Q^{E}}{Q^{S}}\right) \tag{12}$$

This is the crystallization pressure, which is the pressure exerted by the crystal on the surrounding solid matrix. The maximum pressure occurs when a large crystal grows in a pore with small entries, as in Fig. 5b. If the radius r_p is macroscopic, then $\kappa_{CL}^{S} \approx 0$ and $Q^{S} = K$, so Eq. (12) reduces to Correns' equation, Eq. (8), with $Q = Q^{E}$. The compressive stress exerted normal to the confining surface by the crystal produces a tensile stress in the perpendicular direction. If the supersaturation is significant, then the stress can exceed the tensile strength of the body; this is evidently the case for the stones shown in Figs. 3 and 4.

4. The drying front

A porous body typically has interconnected pores with a range of diameters. When the pore liquid begins to evaporate, a meniscus develops in each pore, and the capillary pressure in the pore liquid decreases (i.e., becomes increasingly negative) according to Laplace's equation:

$$p_c = p_e + \gamma_{LV}\kappa_{LV} = p_e + \frac{2\gamma_{LV}}{r_m} \tag{13}$$

where p_e is the equilibrium vapor pressure of a flat surface, γ_{LV} is the liquid/vapor surface energy, and κ_{LV} is the curvature of the meniscus; the second equality applies for a hemispherical meniscus with radius r_m. The curvature of the interface is related to the relative humidity (RH) by [14]

$$p_c - p_e = \frac{2\gamma_{LV}}{r_m} = \frac{R_g T}{V_L} \ln(\mathrm{RH}) \tag{14}$$

where V_L is the molar volume of the liquid. The curvature of the meniscus must be the same in each pore, regardless of its size, or the capillary pressure would induce flow between pores until equilibrium was established; that is, r_m depends on the relative humidity, not on the pore radius, r_p. Consider the simple case shown in Fig. 6, consisting of a large and small pore with radii r_L and r_S, respectively. If the RH is high enough so that

$$\frac{R_g T}{V_L}\ln(\mathrm{RH}) \geq -\frac{2\gamma_{LV}\cos(\theta)}{r_L} \tag{15}$$

where θ is the contact angle between the liquid and solid, then both pores remain full of liquid, as in Fig. 6a. (In the following discussion, we assume that the contact angle is low, as is typically true in cementitious materials and stone.) If the RH drops into the range,

$$-\frac{2\gamma_{LV}\cos(\theta)}{r_L} > \frac{R_g T}{V_L}\ln(\mathrm{RH}) \geq -\frac{2\gamma_{LV}\cos(\theta)}{r_S} \tag{16}$$

then, the larger pore will drain, and a pressure difference will occur between the two pores equal to

$$\Delta p = 2\gamma_{LV}\cos(\theta)\left(\frac{1}{r_L} - \frac{1}{r_{mS}}\right) \tag{17}$$

where r_{mS} is the radius of the meniscus in the small pore. This pressure difference will draw liquid from the larger pore into the smaller one at a rate determined by Eq. (1). If $\theta = 90°$, then, the menisci are flat, and both pores drain simultaneous when RH drops below unity; if $\theta > 90°$, then, the smaller pore drains first. If the RH satisfies

$$\frac{R_g T}{V_L}\ln(\mathrm{RH}) < -\frac{2\gamma_{LV}\cos(\theta)}{r_S} \tag{18}$$

then the small pore should drain when equilibrium is established. Suppose, however, that the large pore has only receded a distance h into the interior, as in Fig. 6b, so that the flux of liquid to the surface is

$$J_C = -\frac{k_S}{\eta}\frac{\Delta p}{h} = \frac{2\gamma_{LV}\cos(\theta)}{h}\frac{k_S}{\eta}\left(\frac{1}{r_{mS}} - \frac{1}{r_L}\right) \tag{19}$$

where k_S is the permeability of the partially saturated network, in which only the smaller pores contain liquid.

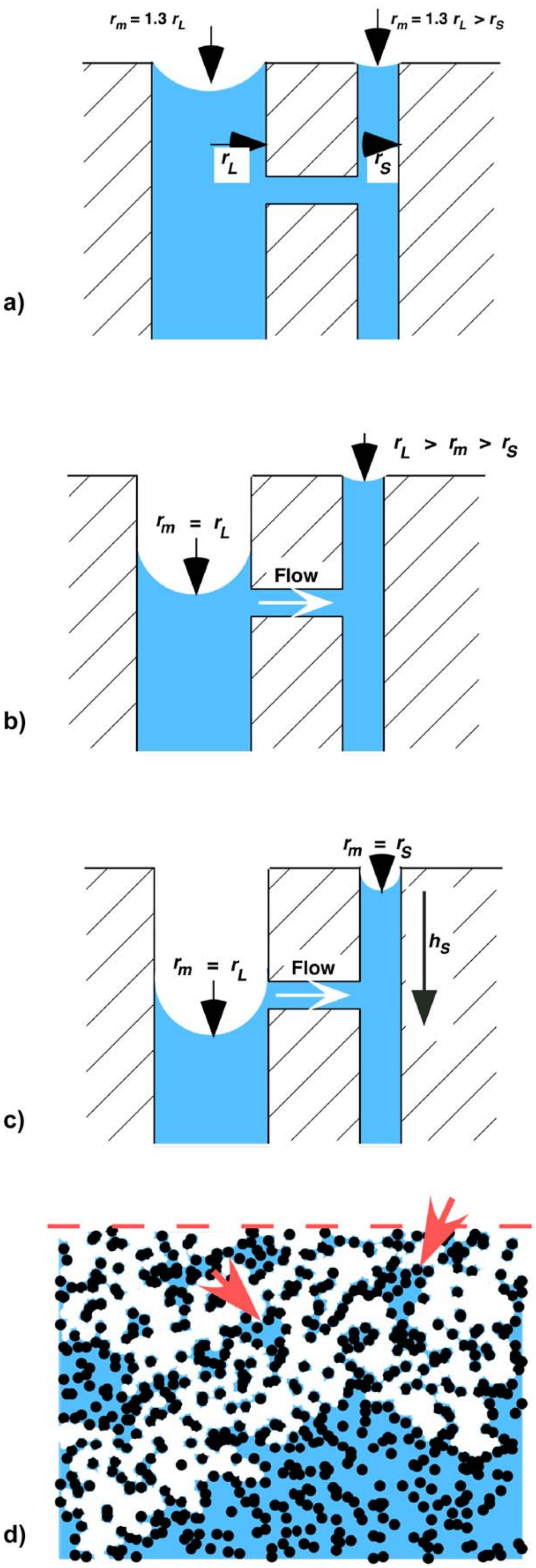

Fig. 6. A large pore (radius r_L) and a small pore (r_S) intersect the surface of a porous body. (a) As liquid evaporates, the radius of the meniscus, r_m, is the same in each pore; otherwise, the difference in capillary pressure would produce flow until the pressures did equilibrate. (b) If the relative humidity is low enough that $r_m < r_L$, the liquid will drain from the large pore into the smaller one. (c) When the depth of the larger meniscus reaches h_S, the flux of liquid into the smaller pore falls below the evaporative flux, and the smaller pore begins to drain. (d) In a material with a broad range of pore sizes, as the drying front advances, there may be pockets of liquid that become isolated because the pore entries on the perimeter of the region are small. When the local RH becomes low enough for the menisci to pass through those pore entries, the pocket will dry up. In this sketch, the black dots represent the cross-section of the solid phase and the shaded region is liquid; the arrows indicate two of the trapped pockets of liquid.

If J_C is greater than the rate of evaporation, J_E, then, the small pore will not drain, and the meniscus at its mouth will acquire only enough curvature to draw a flux matching, J_E. As h increases, the RH near the surface of the meniscus in the large pore rises, so the rate of evaporation from that meniscus will decrease, and most of the drying will occur by evaporation from the smaller meniscus remaining at the outer surface.

As the liquid recedes farther into the large pore, the increase in h reduces the flux J_C, so the radius of the meniscus in the small pore must decrease. The maximum pressure drop occurs when $r_{mS} = r_S$. The small pore will finally drain when the meniscus in the large pore reaches depth h_S, where

$$J_E = \frac{2\gamma_{LV}\cos(\theta)}{h_S}\frac{k_S}{\eta}\left(\frac{1}{r_S} - \frac{1}{r_L}\right) \tag{20}$$

Thus, h_S represents the width of the drying front, which is the distance between the zones that are fully saturated and those that are fully drained [19,20]; the faster the rate of evaporation, the narrower the drying front becomes. If the difference in pore size is great (so that Δp is large) and the small end of the pore size distribution is large (so that k_S is high), then vapor may percolate entirely through the body while the liquid remains in the smaller pores near the drying surface (that is, h_S is larger than the thickness of the body). However, when k_S is small, the front may be narrow even when J_E is low.

In a body with a range of pore sizes, as the drying front advances through the body, there may be pockets of liquid that become isolated, as in Fig. 6c, because the pore entries into those regions are small. Such regions will eventually drain when the local RH is low enough for the menisci to penetrate the pore entries. Crystallization in such pockets is discussed in Section 6. Next, we consider how the crystals will grow as a solution evaporates from the pores.

5. Equilibrium distribution of crystals

When the pore liquid contains salt, the same process of pore drainage will occur, with the result that the concentration of the solution will tend to rise in the smaller pores, from which the liquid is evaporating. Salt is therefore more likely to precipitate in the smaller pores. The homogeneous nucleation of salt requires a high supersaturation; thus, heterogeneous nucleation is much more likely, especially within a porous body whose pore surfaces expose a variety of crystal phases. Suppose that there is a grain with width w_n on the surface of a pore with radius r_p that permits the nucleation of salt, as in Fig. 7. The radius of curvature of the nucleus, r_n, is determined by the contact angle, θ_n, between the salt and the nucleating heterogeneity. If the nucleus is a hemispherical cap with curvature $2/r_n$, then it can form when the supersaturation reaches Q^n, which is found from Eq. (7):

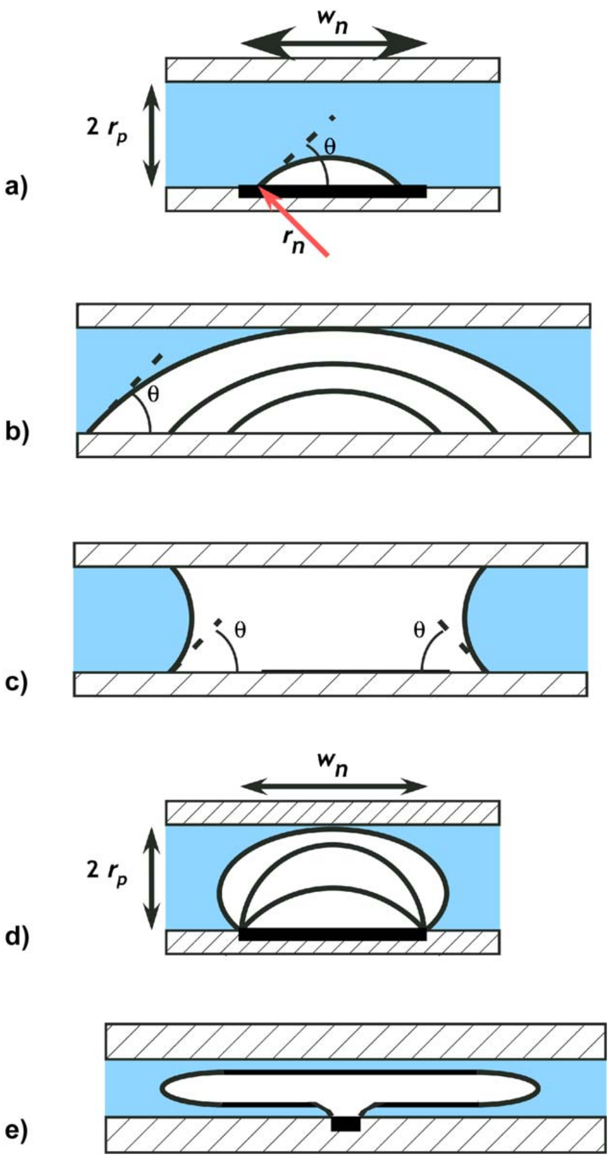

Fig. 7. (a) A salt crystal with radius of curvature r_n forms on a nucleating heterogeneity on the pore wall. (b) If the whole pore wall has a low contact angle with the salt, then the crystal spreads along the wall. (c) Once it touches the other side, a concave meniscus forms on the leading edge, analogous to that of a liquid rising in a capillary. (d) If the wall adjacent to the heterogeneity has a high contact angle with the salt, as is typically the case, the supersaturation must increase to permit the curvature of the crystal/liquid interface to increase. The radius of curvature decreases to $w_n/2$ as the crystal develops into a hemisphere on the nucleating heterogeneity; growth may require a further decrease in radius if $w_n > 2r_n$. (e) If the supersaturation becomes high enough to permit such a crystal to form, it will then grow unstably until its curvature becomes $2/(r_p - \delta)$, as in Fig. 5a.

$$\frac{2\gamma_{CL}}{r_n} = \frac{R_g T}{V_C}\ln\left(\frac{Q^n}{K}\right) \tag{21}$$

The solubility, K, of the crystal is affected by the capillary pressure, p_c, in the liquid [12,21]:

$$p_c = \frac{R_g T}{V_C - \bar{V}_C} \ln\left(\frac{K(p_c)}{K(0)}\right) \tag{22}$$

where $\bar{V}_C$ is the partial molar volume of the crystal in solution. Thus, if $\bar{V}_C < V_C$, so that the salt occupies less volume in solution than in the crystal phase, then the capillary suction ($p_c < 0$) reduces the solubility and conversely.

If the pore surface in Fig. 7a is uniform, offering the same contact angle everywhere, then the crystal will grow spontaneously because when its radius exceeds r_n, it finds itself in a supersaturated solution. Once it touches the opposite wall, as shown in Fig. 7b, it will adopt the same contact angle on that side, so that a concave meniscus forms on the leading edge of the crystal (analogous to that of a liquid rising in a capillary). However, it is far more likely that the crystal will not wet the wall; as mentioned previously, there will typically be a contact angle of 180°, so that a film of liquid is retained between the wall and the crystal. In that case, as the nucleus begins to grow, its radius of curvature must *decrease*. It is clear from an inspection of Fig. 7c that the radius of curvature decreases as the crystal evolves into a hemisphere with diameter equal to the width of the heterogeneity. It will be able to reach that size only if the supersaturation rises enough to satisfy

$$\frac{4\gamma_{CL}}{w_n} = \frac{R_g T}{V_C} \ln\left(\frac{Q}{K}\right) \tag{23}$$

If the pore diameter is smaller than w_n, then the radius of the crystal must decrease until it reaches the pore radius; therefore, the supersaturation must continuously increase. However, if $w_n \ll r_n$, the maximum curvature occurs when the crystal radius equals $w_n/2$; once it reaches that size, it will grow unstably because a crystal with a larger radius is in equilibrium with a supersaturation lower that what is already present. In such a case, dendrites might form with tip radii equal to w_n. The crystal will evolve towards an equilibrium shape, such as in Fig. 5, as the growth of the crystal reduces the supersaturation.

Nucleating heterogeneities are equally likely to be present in pores of all sizes, so the sequence of events in Fig. 7 could occur simultaneously in pores of different sizes. However, as growth consumes the supersaturation, there is a driving force for the smaller crystals to dissolve in favor of larger ones because Eq. (7) indicates that smaller crystals are more soluble. Suppose that crystals have nucleated in two neighboring pores with different sizes and that growth has consumed the supersaturation, to the point that each crystal is in equilibrium with the adjacent solution, according to Eq. (9). This means that the solute content in the smaller pore is higher than that in the larger pore, so the solute will tend to diffuse toward the larger pore. As it does so, the smaller crystal will begin to dissolve, and the larger one will grow as it consumes the ions diffusing to it. This process will result eventually in the transfer of salt to the largest accessible pore (that is, the largest pore that is part of the liquid-filled network). Therefore, there could be a high transient stress from the crystallization pressure while crystals grow under a high supersaturation, then some relaxation as the crystals relocate from the smaller to the larger pores.

In the situation described in Fig. 1, the approach to the equilibrium distribution of salt is complicated by the fact that the precipitation of salt alters the permeability of the body and may entirely block pores near the surface of the wall. Consequently, evaporation slows down, and the liquid rises higher in the wall. Depending on the degree to which the surface is sealed by salt, the solution might even rise to h_{eqm}, given by Eq. (3), before a true steady state is reached and equilibrium is established.

6. Nonequilibrium distribution of salt

Suppose that the solution is trapped in a region of the porous network whose perimeter has small pore-entry radii, as in Fig. 7c. Crystalline salt will gradually redistribute into the larger pores within the saturated region. If the RH drops enough that the menisci can pass through the pore entries, then the liquid will continue to evaporate, and the continuity of the liquid film could be lost, as in Fig. 8. The liquid has evaporated to the extent that the solution only remains between the crystal and the pore wall. As the supersaturation increases further, it cannot be relieved by growth of the free end of the crystal because there is no liquid film that would allow ions to diffuse to the free surface. Under equilibrium conditions, described by Eq. (12), the crystallization pressure is limited by the size of the pore. However, in the nonequilibrium situation shown in Fig. 8, the pressure is limited only by the RH and the disjoining pressure. If the humidity is low enough to permit further evaporation, the crystal finds itself in contact with an increasingly supersaturated solution, but it cannot grow because it is confined by the pore wall; the pressure it

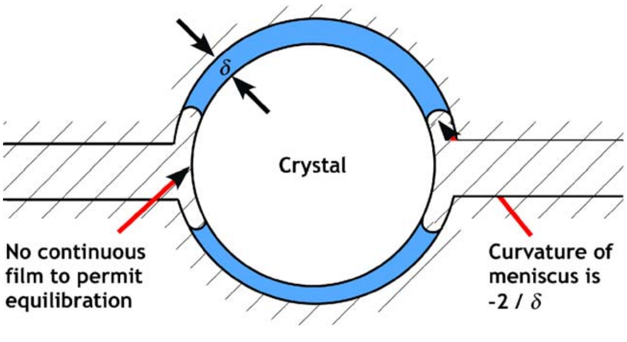

Fig. 8. Drying has proceeded to the point that the meniscus lies between the crystal and the pore wall, so that ions cannot diffuse to the hemispherical end of the crystal; consequently, the supersaturation in the liquid cannot be relieved by further growth.

exerts on the wall will rise until the wall breaks, the salt crystal yields, or the pressure exceeds the disjoining pressure and the crystal is forced into contact with the wall. Yield stresses for salts are high (e.g., 200–350 MPa for alkali halides [22]) compared with the tensile strength of nonmetallic building materials, so damage to the pore wall is the most likely result.

Nonequilibrium growth is not limited to the case of pockets bypassed by the drying front, as in Fig. 8c. It could happen anywhere along the boundary of the zone of subflorescence, shown in Fig. 1, if evaporation raises the concentration of the solution faster than it is reduced by the diffusion of the ions away from the meniscus. This is very important, because it explains how crystallization pressure can cause damage to materials with relatively large pores, such as stone, where the pressures predicted by Eq. (12) are small.

The existence of crystallization pressure in a nonequilibrium system was demonstrated in an ingenious experiment by Taber [16]. He passed cold water through the jacket of a double-walled spherical vessel, and through the inside of the sphere he flowed a solution that was saturated at an elevated temperature. The solution became supersaturated in the cool sphere, so that salt precipitated and gradually filled the sphere. In the zone between the crystal and the glass wall of the sphere, the supersaturated solution forced the crystal to exert pressure on the wall and eventually, the apparatus shattered. In this experiment, the diameter of the inlet tube was large, so that the crystal would have consumed the supersaturation by growing out into the inlet, rather than pressing against the wall, if the temperature had been uniform. However, the inlet was warm and therefore the solution was not supersaturated at that point. The supersaturation was limited to the cold region near the wall of the vessel, so this was a case of nonequilibrium growth, which permitted high stress to be generated by a large crystal.

7. Cyclic wetting and drying

When water is introduced into a porous body by rain or sea spray, rather than capillary rise, the pattern of crystallization is different. In such cases, the salt may be inherent to the porous material (e.g., gypsum in Portland cement) or result from the reaction with atmospheric pollutants such as sulfates that react with limestone to form gypsum [1,23]. Each time a wave breaks on the sea, it throws up droplets of water that may dry into fine grains of salt, which can be transported kilometers inland by the wind and be deposited on buildings [24]; rain dissolves the salt, which is then absorbed into the wall by capillary suction. The subsequent evaporation of water and the nucleation and growth of salt follow the same principles described previously, but the processes occur closer to the surface, and the formation of isolated pockets of salt is more likely.

A case of particular interest is the damage done by sodium sulfate, which is one of the most destructive salts [24]. This salt exists as an anhydrate called thenardite, Na_2SO_4, or as a decahydrate called mirabilite, $Na_2SO_4 \cdot 10H_2O$; at room temperature, mirabilite decomposes to thenardite at RH $< 75\%$ [25]. If a solution of this salt dries at temperatures below 32 °C, mirabilite is expected to precipitate, then transform to thenardite, if the RH is low enough. A standard test for salt durability is to soak a piece of stone is a solution of sodium sulfate, then dry it, and repeat until damage is observed [26]. Surprisingly, the damage is found to occur during the wetting cycle, rather than drying. Many authors attribute the damage to hydration pressure, which is the pressure that would be required to prevent the 314% increase in molar volume as the anhydrate transforms to the decahydrate. However, this is not a meaningful idea because thenardite cannot absorb water continuously as it hydrates and expands like a sponge; instead, thenardite dissolves and reprecipitates as mirabilite [27]. Thus, the damage actually results from the crystallization pressure exerted by mirabilite [28]. The mechanism is rather subtle [29,30]: the invading water encounters thenardite and dissolves the salt until the solution is saturated with respect to that crystal, but at ambient conditions a solution that is saturated with thenardite is highly supersaturated with respect to mirabilite. This novel method for producing a high supersaturation is what is responsible for the unusual destructiveness of this salt. This mechanism is not acting in the experiments shown in Figs. 3 and 4, where there is a steady supply of solution. However, it does act whenever a sodium-sulfate-containing body is subjected to cycles of wetting and drying.

8. Growth of ettringite

Gypsum is added to Portland cement to encourage the growth of the trisulfate mineral ettringite, $Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$ [31], during the initial hydration reaction and thereby prevent premature setting [32]. However, when ettringite precipitates after the concrete has hardened (called delayed ettringite formation or DEF), it is blamed for causing damage [33]. There is some controversy as to whether the expansion and cracking that accompany DEF results from the acicular crystals that form around the aggregates [34] or from the precipitation in the smaller pores of the cement paste [35]. The preponderance of evidence seems to support the idea that crystallization pressure develops in the nanometric pores of the paste, producing an expansion of the paste and opening gaps around the aggregate, followed by the precipitation of crystals in the gaps [36]. The supersaturation necessary to produce the pressure results from heating to a temperature high enough (approximately 70 °C) to destabilize ettringite with respect to monosulfate phases, followed by cooling. Upon cooling to 20 °C, the supersaturation is estimated to be $Q/K \approx 30$ [37], which could produce a crystallization pressure of about 6 MPa, well in excess of the tensile strength of cement paste or concrete. Assuming a crystal/liquid energy of about 0.1 J/m^2, this supersaturation would allow the crystals of ettringite to penetrate any pore with a radius exceeding 15 nm; such crystals would be too small to be detected by X-ray diffraction or scanning electron microscopy.

A detailed discussion of the development of stress during the precipitation of ettringite, presented in Ref. [38], leads to the following conclusions. (a) High supersaturation results upon cooling from above 70 °C to room temperature, so that crystallization pressure can exceed the tensile strength. (b) Crystals large enough to be observed by SEM are not capable of generating significant stress, so the crystals responsible for expansion and cracking are the ones that cannot be seen. (Their presence can, however, be detected by chemical analysis of the paste [36,39].) (c) There is a competition between the growth of the stressed crystals in mesopores and the unstressed crystals in macropores. The crystallization pressure is expected to build as small crystals grow under high supersaturation, then diminish as they dissolve and transfer the solute to larger crystals. Damage is expected only during the transient period of elevated stress. (d) The duration of this transient may be short compared with the period over which growth of ettringite produces large strains. DEF is reported to produce strains on the order of 1% over a period of months or years. However, cement paste or concrete cannot sustain tensile strains even as large as 0.1% without cracking; hence, most of the DEF strain occurs *after* the material is severely damaged, and the subsequent expansion can therefore occur under small applied stresses. In materials exhibiting expansion from DEF, the period of high stress during which the initial damage is done (i.e., while the strain rises toward approximately 0.1%) is relatively short (typically a few weeks). We do not yet have sufficient data to permit the accurate modeling of the kinetics of desorption and diffusion of solute leading to nucleation and growth of ettringite. However, if the diffusion of ions occurs within the inner product of calcium–silicate–hydrate (C–S–H), then the diffusion coefficient would be on the order of $D \approx 10^{-13}$ m^2/s [40]. The distance, x, over which the composition can be homogenized by diffusion in time t, is $x^2 \approx Dt$, so we estimate that $x \approx 400$ μm in 20 days. Therefore, if the distance from the mesopores containing crystals to the macroscopic sinks is a few hundred microns, the transient stress can last a matter of weeks.

9. Growth of C–S–H

In a recent review, Acker [41] summarizes the evidence of several studies indicating that the hydration of cement results in crystallization pressure. For example, Miyazawa and Monteiro [42] prepared a set of samples with water/cement ratio = 0.3 that varied in thickness from 13 to 102 mm. As shown in Fig. 9, the thin samples expanded, while the thicker ones initially contracted and later expanded. Acker [41] argues that the expansion results from the crystallization pressure generated during the hydration of Portland cement, which is opposed by capillary pressure created by the self-desiccation of the paste. In the thin samples, water is able to enter from the environment to prevent the development of significant capillary pressure, so the crystallization pressure dominates, and the sample expands. In thicker samples, the kinetics of penetration of water are slow enough that the capillary pressure overcomes the crystallization pressure, and the sample contracts; later on, even the large samples expand as the rate of reaction decreases and the water gradually penetrates the pores. Experiments of this kind, if combined with measurements of creep rate and degree of hydration, could be used to quantify the pressure generated during hydration.

The origin of the crystallization pressure in this case is not clear. There is a large increase in volume as a cement particle transforms from a mixture of di- and tricalcium silicate (among other phases) into C–S–H. However, given that the C–S–H forms a binding phase, it is improbable that there could be a significant disjoining force between surfaces of C–S–H particles. Therefore, crystallization pressure is not expected to arise from the mutual repulsion of surfaces of the hydrates. However, if a single particle of cement forms a coating of hydration products, how is the expansion of the unhydrated core accommodated when it finally reacts? The situation is analogous to a droplet of water that forms a crust of ice on its surface: the freezing of the liquid inside the crust involves a volumetric expansion, so it cannot freeze unless the crust stretches or breaks. (This is the phenomenon responsible for the bump on the top of an ice cube.) Similarly, hydration of the interior of the cement

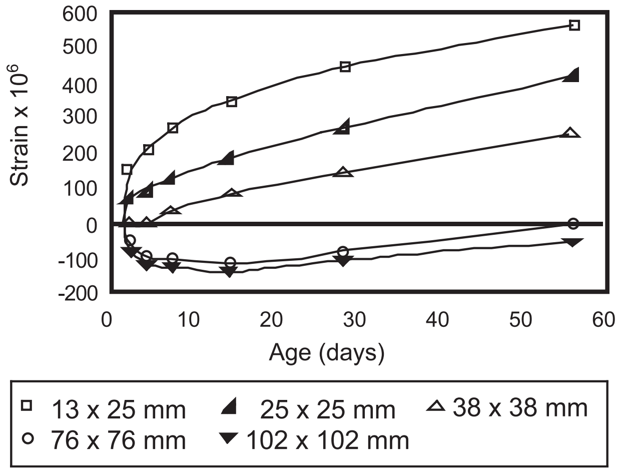

Fig. 9. Strain measured during hydration of Type I Portland cement paste, made with a water/cement ratio of 0.30, during storage in a fog room (100% RH). Smaller samples expand, while thick samples initially contract. From Ref. [42].

particle requires that the existing coating split or stretch, or that the ions diffuse from the cement particle to the exterior and deposit there. Therefore, some of the observed expansion might result from hydration, not because the particles repel one another, but because the core of each particle is expanding. There is also likely to be crystallization pressure during hydration, owing to precipitation of substantial quantities of ettringite and calcium hydroxide, and these are likely to generate a significant disjoining pressure.

10. Conclusions

A necessary condition for the occurrence of crystallization pressure is the presence of supersaturation (for precipitation) or undercooling (for freezing), but that is not sufficient. There must also be a disjoining pressure between the growing crystal and any confining surface; otherwise, the crystal will come into direct contact with the obstacle and stop growing. However, if there is a repulsive force between the surfaces, then the crystal will retain a liquid film between itself and the obstacle and try to push it away with a force that depends on the driving force for growth. When the solution surrounds the crystal, it will remain in mechanical equilibrium, so the force exerted on the confining walls will depend on the curvature of the crystal. In such cases, stresses in the megapascal range are only expected in nanometric pores. However, the liquid film may be disrupted during drying that the solution is trapped between the surface of the crystal and the pore wall; then, the supersaturation cannot be relieved by growth and stress comparable with the disjoining pressure can be exerted even in large pores.

Supersaturation of salts can result from capillary rise and evaporation, or from cycles of wetting and drying. Sodium sulfate generates very high supersaturation by a different route: when the anhydrate dissolves under ambient conditions, the resulting solution is highly supersaturated with respect to the decahydrate phase. This phenomenon makes sodium sulfate one of the most destructive salts in nature. In the case of ettringite, treatment at elevated temperature followed by cooling to room temperature generates supersaturation sufficient to produce crystallization pressure well in excess of the tensile strength of concrete.

Acknowledgements

The author is indebted to Frans Spaepen (Harvard University) and John Cahn (NIST) for helpful discussions of surface free energy.

References

[1] E.M. Winkler, Stone in Architecture, 3rd. ed., Springer, Berlin, 1997, Ch. 6.
[2] D. Camuffo, Microclimate for Cultural Heritage, Elsevier, Amsterdam, 1998.
[3] J. Happel, H. Brenner, Low Reynolds Number Hydrodynamics, Martinus Nijhoff, Dordrecht, 1986.
[4] C.J. Ridgway, P.A.C. Gane, J. Schoelkopf, Effect of capillary element aspect ratio on the dynamic imbibition within porous networks, J. Colloid Interface Sci. 252 (2002) 373–382.
[5] N.R. Buenfeld, M.T. Shurafa-Daoudi, I.M. McLoughlin, Chloride transport due to wick action in concrete, in: L.O. Nilsson, M.P. Olliver (Eds.), Chloride Penetration into Concrete, RILEM, Paris, 1997, pp. 315–324.
[6] R. Snethlage, E. Wendler, Moisture cycles and sandstone degradation, in: N.S. Baer, R. Snethlage (Eds.), Saving our Cultural Heritage: The Conservation of Historic Stone Structure, Wiley, New York, 1997, pp. 7–24.
[7] K. Zehnder, A. Arnold, Crystal growth in salt efflorescence, J. Cryst. Growth 97 (1989) 513–521.
[8] N. Yellin, L. Ben-Dor, N. Zelingher, Whisker growth by means of porous glass, J. Mater. Sci. 21 (1986) 2648–2650.
[9] S.Z. Lewin, The mechanism of masonry decay through crystallization, Conservation of Historic Stone Buildings and Monuments, National Acad. Press, Washington, DC, 1982, pp. 120–144.
[10] S. Mindess, J.F. Young, Concrete, Prentice-Hall, Englewood Cliffs, NJ, 1981.
[11] G.W. Scherer, Crystallization in pores, Cem. Concr. Res. 29 (8) (1999) 1347–1358; Reply to discussion of Crystallization in pores, Cem. Concr. Res. 30 (4) (2000) 673–675.
[12] G.W. Scherer, Stress from crystallization of salt in pores, in: V. Fassina (Ed.), Proc. 9th Int. Cong. Deterioration and Conservation of Stone, vol. 1. Elsevier, Amsterdam, 2000, pp. 187–194.
[13] J.W. Cahn, Surface stress and the chemical equilibrium of small crystals: I. The case of the isotropic surface, Acta Metall. 28 (1980) 1333–1338.
[14] A.W. Adamson, Physical Chemistry of Surfaces, 5th ed., Wiley, New York, 1990.
[15] C.W. Correns, Growth and dissolution of crystals under linear pressure, Discuss. Faraday Soc. 5 (1949) 267–271.
[16] S. Taber, The growth of crystals under external pressure, Am. J. Sci. 41 (1916) 532–556.
[17] G.F. Becker, A.L. Day, Note on the linear force of growing crystals, J. Geol. XXIV (4) (1916) 313–333.
[18] A.E. Corte, Vertical migration of particles in front of a moving freezing plane, J. Geophys. Res. 67 (3) (1962) 1085–1090.
[19] M.J. Cima, J.A. Lewis, A.D. Devoe, Binder distribution in ceramic greenware during thermolysis, J. Am. Ceram. Soc. 72 (7) (1989) 1192–1199.
[20] G.W. Scherer, Fundamentals of drying and shrinkage, in: V.E. Henkes, G.Y. Onoda, W.M. Carty (Eds.), Science of Whitewares, Am. Ceram. Soc., Westerville, OH, 1996, pp. 199–211.
[21] F.T. Wall, Chemical Thermodynamics, Freeman, San Francisco, 1965, p. 353.
[22] M.F. Ashby, D.R.H. Jones, Engineering Materials 1, 2nd ed., Butterworth, Oxford, 1996.
[23] K. Lal Gauri, J.K. Bandyopadhyay, Carbonate Stone, Chemical Behavior, Durability and Conservation, Wiley, New York, 1999.
[24] A. Goudie, H. Viles, Salt Weathering Hazards, Wiley, Chichester, 1997.
[25] N. Tsui, R.J. Flatt, G.W. Scherer, Crystallization damage by sodium sulfate, J. Cult. Herit. 4 (2003) 109–115.
[26] C.A. Price, The use of the sodium sulphate crystallisation test for determining the weathering resistance of untreated stone, Deterioration and Protection of Stone Monuments, RILEM, Paris, 1978, pp. Price-1–Price-24.
[27] E. Doehne, In situ dynamics of sodium sulfate hydration and dehydration in stone pores: observations at high magnification using the environmental scanning electron microscope, in: V. Fassina, H. Ott, F. Zezza (Eds.), III Int. Symp. Conservation of Monuments in the Med-

iterranean Basin, Venice, Soprintendenza ai beni artistici e storici di Venezia, Venezia, 1994, pp. 143–150.

[28] R.J. Flatt, G.W. Scherer, Hydration and crystallization pressure of sodium sulfate: a critical review, in: P.B. Vandiver, M. Goodway, J.L. Mass (Eds.), Materials Issues in Art & Archaeology VI, MRS Symposium Proc., vol. 712, Materials Res. Soc., Warrendale, PA, 2002, pp. 29–34.

[29] S. Chatterji, A.D. Jensen, Efflorescence and breakdown of building materials, Nord. Concr. Res. 8 (1989) 56–61.

[30] R.J. Flatt, Salt damage in porous materials: how high supersaturations are generated, J. Cryst. Growth 242 (2002) 435–454.

[31] R. Berliner, The structure of ettringite, in: M. Cohen, S. Mindess, J. Skalny (Eds.), Materials Science of Concrete—Sidney Diamond Symposium, Am. Ceram. Soc., Westerville, OH, 1998, pp. 127–141.

[32] S. Mindess, J.F. Young, Concrete, Prentice-Hall, Englewood Cliffs, NJ, 1981.

[33] B. Erlin (Ed.), Ettringite—The Sometimes Host of Destruction, ACI, Farmington Hills, MI, 1999, SP-177, 265 pp.

[34] D. Bonen, S. Diamond, Characteristics of delayed ettringite deposits in ASR-affected steam cured concretes, in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-based Systems, E & FN Spon, London, 1997, pp. 277–304.

[35] V. Johansen, N. Thaulow, Heat curing and late formation of ettringite, in: B. Erlin (Ed.), Ettringite—The Sometimes Host of Destruction, ACI, Farmington Hills, MI, 1999, pp. 47–64, SP-177.

[36] H.F.W. Taylor, C. Famy, K.L. Scrivener, Delayed ettringite formation, Cem. Concr. Res. 31 (2001) 683–693.

[37] R.J. Flatt, G.W. Scherer, Thermodynamics of crystallization stresses in DEF, in preparation.

[38] G.W. Scherer, Factors affecting crystallization pressure, in: K.L. Scrivener, J. Scrivener (Eds.), Internal Sulfate Attack: Proceedings of RILEM Workshop on Delayed Ettringite Formation, RILEM publications, Paris, 2004.

[39] K.L. Scrivener, M.C. Lewis, Effect of heat curing on expansion of mortars and composition of calcium silicate hydrate gel, in: B. Erlin (Ed.), Ettringite—The Sometimes Host of Destruction, ACI, Farmington Hills, MI, 1999, pp. 93–104, SP-177.

[40] J. Marchand, personal communication.

[41] P. Acker, Swelling, Shrinkage and Creep: Mechanical Approach to Cement Hydration, Materials and Structures, 37 (265) (2004).

[42] S. Miyazawa, P.J.M. Monteiro, Volume change of high-strength concrete in moist conditions, Cem. Concr. Res. 26 (4) (1996) 567–572.