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Discussion

Reply to the discussion by S. Chatterji of the paper, "*Crystallization in pores*"☆

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I thank Dr. Chatterji for his comments [1] on my paper [2]. The main thrust of his remarks is that many other mechanisms contribute to damage of concrete and masonry, and that some of them can be more important than crystallization pressure. I do not disagree with that contention at all. Evidently, I should have stated explicitly that the purpose of my paper was not to catalog and explain all mechanisms of deterioration, nor even to deal with all aspects of crystallization pressure, but simply to examine in detail the thermodynamic aspects of the problem, and to draw some insight regarding the mechanisms of damage caused by *pressure exerted directly by crystals on the solid phase*. In particular, I made no mention of kinetic aspects of crystal growth, which is obviously of importance with respect to ice formation, since the growth rate affects the magnitude of the hydraulic pressure. Certainly, discussions of wetting and drying, sulfate attack, alkali–silica reaction, and other mechanisms of deterioration cited by Dr. Chatterji were outside the scope of my paper.

I did not say, nor did I intend to imply, that the concept of crystallization pressure can be used "without discrimination" to explain damage from salt and ice. There are important similarities with respect to the crystallization pressure in those two cases, as detailed in my paper. However, ice formation is distinguished from salt crystallization by several obvious features: all of the water can transform into ice, whereas the amount of salt that forms from a solution is relatively small; ice growth is rapid compared to precipitation of salt, and the volume increase can create significant hydraulic pressure, as pointed out by Powers [3]; temperature gradients extend deeply into a body, whereas concentration gradients created by evaporation are relatively superficial. Therefore, one must certainly discriminate between those processes to understand the nature of the damage they cause. Nevertheless, with respect to crystallization pressure, there are important similarities with regard to the role of interfacial energies, pore size distribution, percolation of crystals, and so on, on the magnitude of the stress.

Dr. Chatterji points out that damage caused by efflorescence of crystals is limited to a superficial zone with a thickness of millimeters. To clarify the terminology, let me point out that efflorescence, which is the growth of crystals at the exterior surface of a porous body, does not cause any damage. It is *subflorescence*, which is the growth of crystals within the pores that can cause damage from crystallization pressure. The transition from efflorescence to subflorescence occurs when the rate of evaporation exceeds the rate at which the solution arrives at the surface, so that the liquid/vapor interface retreats below the surface [4]. The reason why the damage is limited to a superficial layer is simply that this is the region where evaporation creates a high driving force for growth. Buenfeld et al. [5] have analyzed the kinetics of transport of a solution to a surface where evaporation occurs, taking account of flow of the liquid, diffusion of the salt within the liquid, and evaporation at the surface. If the evaporation rate is high enough to cause subflorescence, the concentration of salt peaks just below the surface, and that is where crystallization pressure is generated.

To explain the destruction of the surface layer by subflorescence, Dr. Chatterji speculates on the distribution of critical flaws, and the possibility that crystallization pressure acts on subcritical flaws. To clarify this point, we clearly need to define what a critical flaw means. In Ref. [2], I argued that crack growth occurs only when the stress field generated by the crystallized region extends far enough to interact with a critical flaw (note that this does not mean that the crystallized region must *contain* a flaw, only that it be nearby). The situation is indicated schematically in Fig. 1, where the tensile stress, σ_θ, from a region of crystallization extends over a volume containing two flaws with different sizes, c_1 (large) and c_2 (small). According to linear elastic

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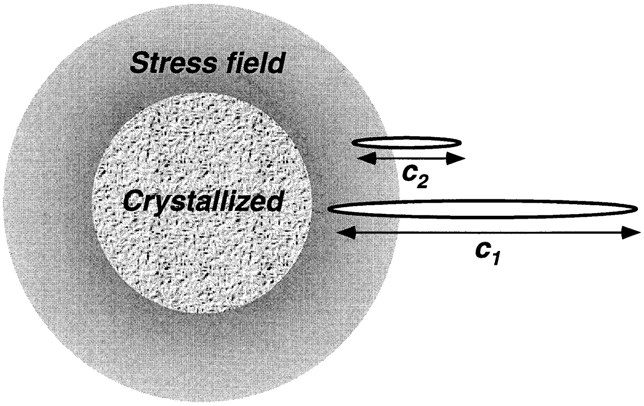

Fig. 1. In the spherical region labelled "Crystallized," the crystals have propagated throughout the pore space, generating tensile circumferential stress (crystallization pressure) that extends throughout the region labelled "Stress field"; the stress is greatest at the edge of the crystallized region and diminishes with distance as $1/r^3$ (as indicated schematically by the gradient in color). The stress acts on a large flaw (length c_1) and a small flaw (length c_2).

fracture mechanics, the critical condition for stability of a crack is given by [6]

$$\sigma_\theta = \frac{K_{Ic}}{Y\sqrt{\pi c}} \tag{1}$$

where K_{Ic} is the critical stress intensity factor (which is a property of the porous matrix), c is the flaw length, and Y is a constant that depends on the shape of the flaw and the specimen. (In fact, concrete is only quasi-elastic, but that is not important for the present discussion.) When Eq. (1) is exactly satisfied, the crack is stable, but if σ_θ is larger than the right side of Eq. (1), then the crack will grow; thus, for a given value of σ_θ, a critical flaw is one that grows and a subcritical flaw is one that does not. If σ_θ is not large enough to cause either crack in Fig. 1 to grow, then they are both (by definition) subcritical flaws; if only c_1 is large enough to satisfy Eq. (1), then it is critical, but c_2 is not. The magnitude of the stress is controlled by the supersaturation and the pore size of the matrix, as explained in Ref. [2]. During a period of slow evaporation, only the larger pores will fill with salt and crystallization pressure will generate small stresses; in that case, only the larger flaws will grow (or perhaps, none will). However, the same material could develop higher crystallization stresses under conditions leading to higher supersaturation (e.g., faster evaporation, slower supply of groundwater, lower temperature); in that case, existing flaws with a range of sizes could satisfy Eq. (1).

The tensile strength of a macroscopic sample of concrete is in the order of 3 MPa, and the flaws that reduce its strength to that low level are quite large; therefore, if the crystallization pressure is only able to generate 3 MPa of stress, then the crystallized region must be large enough (probably tens or hundreds of microns) so that its stress field extends over those large flaws. On the other hand, if the crystallization pressure is large, then it can cause propagation of much smaller flaws. For example, if the supersaturation were so large that the crystal could create tens of megapascals of pressure, then the "critical flaws" (i.e., those that can grow under the applied stress) might be only a few microns long. In that case, the growth of cracks could begin when the crystallized region is comparably small. For the case of subflorescence described by Dr. Chatterji, the fact that the surface was reduced to powder in a superficial layer implies that the supersaturation was high in that region, so that relatively small flaws could grow.

In connection with Eq. (18) of Ref. [2], it was careless of me to say that one could "easily" achieve two-fold supersaturation of NaCl solutions. First of all, that equation is written in the form appropriate for solutions of molecular materials, such as sugar in water. For a monovalent electrolyte, such as NaCl, it should be

$$p_c = p_l + \frac{R_g T}{v_c}\ln(a_{Na^+}a_{cl^-}) \tag{2}$$

where a_{Na^+} and a_{cl^-} are the activities of the sodium and chloride ions, respectively, in solution. To achieve the equivalent of $C/C_0 = 2$ in Eq. (18) of Ref. [2], we require $a_{Na}{}^+ = a_{cl}{}^- = \sqrt{2}$ in Eq. (1). For an ideal solution, this would require a mole fraction of NaCl equal to $C = \sqrt{2}\ C_0$, but when Pitzer's model [7] is used to take account of the non-ideality of the NaCl solution, it appears that one only needs $C \approx 1.3\ C_0$ [8]. The latter value is in the range of the experimental values reported by Dr. Chatterji, so it is possible (if not easy) to produce high crystallization pressures from NaCl. Indeed, NaCl is identified as a major agent of destruction of masonry in the Mediterranean basin [9]. However, it is also true that NaCl is less destructive than sodium sulfate [10]. Although it is often conjectured that the damage from the sulfate is caused by hydration (as anhydrous thenardite transforms to mirabilite by acquiring 10 molecules of water), direct observation in the environmental SEM [11] shows that this is unlikely: thenardite does not swell by acquiring water of hydration; instead, it dissolves and then the mirabilite precipitates from solution. The reason that the sulfate generates more destructive crystallization pressure than the chloride maybe related to the observation that NaCl crystals nucleate at the water/air interface, whereas mirabilite crystals grow under the surface of the liquid [10]. This indicates that the sulfate crystals have a strong tendency to preserve a liquid film at their surface, so they are more likely to reject the pore wall than the chloride crystals. That is, the energy of the interface between stone and mirabilite is probably greater than that between stone and halite, so the former can generate more stress before being forced into contact with the pore wall.

Dr. Chatterji argues that the slow rate of cooling in the field makes it unlikely that large undercoolings could develop in water inside pores, but that is not true. Even when ice forms near 0°C at the surface of a body, it cannot penetrate the pores until the temperature drops enough to satisfy the Gibbs–Thompson equation (Eq. (6) of Ref. [2]):

$$\Delta T = \frac{\gamma_{CL}\kappa_{CL}}{\Delta S_{fv}} = \frac{2\gamma_{CL}}{r\Delta S_{fv}} \tag{3}$$

where ΔT is the depression of the melting point caused by the curvature, κ_{CL}, of the crystal/liquid interface, γ_{CL} is the crystal/liquid interfacial energy, and ΔS_{fv} is the entropy of fusion per unit volume of ice; the second equality applies to a spherical surface with radius r and curvature $\kappa_{CL} = 2/r$. The smaller the pores at the surface, the lower the temperature must become before ice can invade; if the mean pore size (i.e., the breakthrough radius) is 10 nm, then T must be about $-7°C$, but if it is 70 nm, then ice will enter the body at $-1°C$. Mercury intrusion data indicate that the breakthrough radius (i.e., the inflection point on the penetration curve) is smaller than 50 nm for cement paste with water/cement ratio $\leq$ 0.4, so there is a substantial portion of the pore volume that cannot be invaded by ice until the undercooling is 5–10°C.

Dr. Chatterji contrasts the internal cracking caused by ice with the superficial damage caused by subflorescence and concludes that different processes must be at work. In some cases, this is probably true. However, there are certainly crystallization processes by which ice causes superficial damage (viz., scaling [12]) and salt causes internal damage [9]. In general, one expects superficial damage from salt, because the supersaturation, which is the driving force for growth, is greatest at the point where evaporation occurs (viz., at the external surface). In contrast, the undercooling extends deeply into a body in the field, so high crystallization pressures can be created far below the surface. Dr. Chatterji's suggestion that high pressures are created by water trapped within a shell of ice is an interesting one that I analyzed in a previous paper [13]. However, that mechanism is not the only one that can account for internal cracking; if the interior of the body is subjected to high levels of saturation with water and low temperatures, then high crystallization pressures can occur deep within the body.

In summary, crystallization pressure is only one of the many mechanisms that contribute to deterioration of stone and masonry. Crystallization of salt can generate significant pressures if the supersaturation is high, but only if the interfacial energy between the salt and the pore wall is also high, and the pores are small. These circumstances are most likely to occur near the exterior surface, where evaporation can produce high supersaturations; however, the solubility of some salts has a strong dependence on temperature, so temperature variations can produce high supersaturations well inside the body. The growth of ice can generate high pressure by several mechanisms, including direct pressure of the crystal against the wall (which was the exclusive subject of Ref. [2]), hydraulic pressure caused by the change in volume, and confinement of water within a frozen crust. For crystallization pressure to be the cause of damage, crystals must propagate through the pore space and generate stress over a volume large enough to contain flaws. The greater the crystallization pressure, the smaller the flaws that will grow; the largest flaws in concrete (which are probably tens to hundreds of microns long) are activated by relatively low stresses, but only after the crystals have propagated over comparably large distances.

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