Advances in Understanding Damage by Salt Crystallization

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CONSPECTUS

The single most important cause of the deterioration of monuments in the Mediterranean basin, and elsewhere around the world, is the crystallization of salt within the pores of the stone. Considerable advances have been made in recent years in elucidating the fundamental mechanisms responsible for salt damage. As a result, new methods of treatment are being proposed that offer the possibility of attacking the cause of the problem, rather than simply treating the symptoms. In this Account, we review the thermodynamics and kinetics of crystallization, then examine how a range of technological innovations have been applied experimentally to further the current understanding of in-pore crystallization. We close with a discussion of how computer modeling now provides particularly valuable insight, including quantitative estimates of both the interaction forces between the mineral and the crystal and the stresses induced in the material.

Analyzing the kinetics and thermodynamics of crystal growth within the pores of a stone requires sensitive tools used in combination. For example, calorimetry quantifies the amount of salt that precipitates in the pores of a stone during cooling, and dilatometric measurements on a companion sample reveal the stress exerted by the salt. Synchrotron X-rays can penetrate the stone and identify the metastable phases that often appear in the first stages of crystallization. Atomic force microscopy and environmental scanning electron microscopy permit study of the nanometric liquid film that typically lies between salt and stone; this film controls the magnitude of the pressure exerted and the kinetics of relaxation of the stress. These experimental advances provide validation for increasingly advanced simulations, using continuum models of reactive transport on a macroscopic scale and molecular dynamics on the atomic scale.

Because of the fundamental understanding of the damage mechanisms that is beginning to emerge, it is possible to devise methods for protecting monuments and sculptures. For example, chemical modification of the stone can alter the repulsive forces that stabilize the liquid film between the salt and mineral surfaces, thereby reducing the stress that the salt can generate. Alternatively, molecules can be introduced into the pores of the stone that inhibit the nucleation or growth of salt crystals. Many challenges remain, however, particularly in understanding the complex interactions between salts, the role of metastable phases, the mechanism of crack initiation and growth, and the role of biofilms.

Introduction

The longevity of many historic monuments and sculptures is threatened by diverse weathering processes, prominent among which is the stress exerted by salts crystallizing in the pores of the stone.[1,2] A great effort has been made in recent

decades to understand the mechanism of damage responsible for salt weathering,[3−10] as well as to develop methods to prevent damage (see review ref 11). Salt weathering of stone (and of other construction materials and rocks) results from the combined action of salt transport through the porous network and the in-pore crystallization under changing environmental conditions. The crystallization pressure exerted by the crystals on the pore surface is the main agent responsible for damage.

After a brief review of equilibrium and nonequilibrium thermodynamics and of the kinetics of crystallization, we describe how the knowledge about in-pore crystallization has enormously benefited from the technological progress in recent years. The last section presents theoretical advances that have brought new insights into the understanding of in-pore crystallization by providing quantitative estimates of interaction forces between mineral and crystal and of the stress induced in the material.

## Thermodynamics and Kinetics of in-Pore Salt Crystallization

Salt crystallization from a solution begins with the nucleation step, where the solute molecules dispersed in the solvent start to gather into clusters on the nanometer scale. A good background on the theory of nucleation is given by Christian.[12]

The driving force for crystallization is the difference between the chemical potentials of ions in solution and nuclei, $\Delta\mu$, which is directly related to the supersaturation, β, of the salt in the solution. The supersaturation gives the ratio between the ion activity product in solution and the solubility constant of the salt. If β is larger than a threshold value, called supersolubility, nucleation starts abruptly. The threshold supersaturation can be determined experimentally by Nuclear Magnetic Resonance (NMR)[13] and by differential scanning calorimetry for cooling-induced crystallization.[7] Salts with large crystal−liquid interfacial energy (γ_{cl}) and molar volume require a higher supersolubility for nucleation to start and are more prone to cause damage.

The rate of heterogeneous nucleation[12] in a solution (per unit area of substrate per unit time), I^{β}, decreases with increasing viscosity of the solution, η:

$$I^{\beta} = \frac{kT}{\pi\Omega^{5/3}\eta} \exp\left(-\frac{256\gamma_{cl}^{3}\Omega^{2}}{27(kT)^{3}(\ln\beta)^{2}}f(\theta)\right) \quad (1)$$

where k is the Boltzmann constant, T is the temperature, Ω is the volume of a formula unit (i.e., molar volume divided by Avogadro's number), and θ is the contact angle between crystal and substrate. Heterogeneous nucleation on a solid sub-
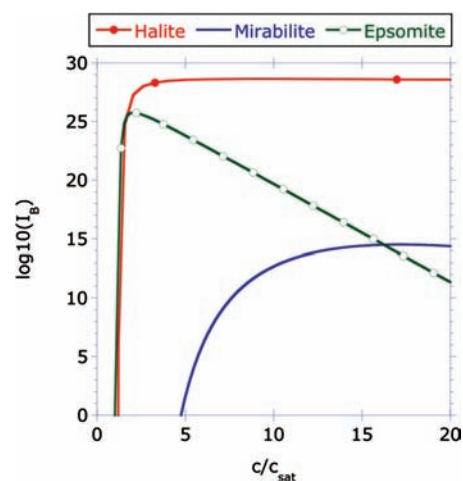
FIGURE 1. Nucleation rate of epsomite, mirabilite, and halite as a function of the ratio between concentration, c, and solubility, c_{sat}, assuming heterogeneous nucleation ($\theta = 1$ rad, $T = 23$ °C), calculated from eq 1.

strate decreases the energy barrier, because the atomic configuration of the substrate is similar to that of the crystal, in contrast to homogeneous nucleation. The reduction of the energy is proportional to a function of the contact angle, $f(\theta)$, that results from the mechanical equilibrium of the interfaces between the substrate, the liquid, and the crystal.

Figure 1 shows the nucleation rate of three different salts at 23 °C as a function of the ratio between molality, c, and solubility, c_{sat}. The supersaturation in eq 1 was calculated considering the nonideality of the solutions.[14] The measured liquid−crystal interfacial energy γ_{cl} of halite (NaCl) is 0.038 N/m,[15] while no experimental value was found for mirabilite and epsomite. A rough estimation was made by analogy to Turnbull's theory[16] relating interfacial energy to the heat of fusion. We assumed that the surface energy is a fraction of the differential heat of dissolution at saturation, ΔH_{d}, gained on moving an ion from the interior of a crystal into the liquid phase, this fraction being dependent on the coordination number of the ions in the crystal, and at its surface (here 0.17). This only applies if the fraction of bonds made by the surface ions with the solution is equal to the fractions of bonds broken in the crystal, which is indeed unknown for most salts. Hence, γ_{cl} of mirabilite ($Na_2SO_4 \cdot 10H_2O$) equals 0.043 N/m for $\Delta H_{d} = 73.5$ kJ/mol estimated with the Pitzer model.[6] For epsomite ($MgSO_4 \cdot 7H_2O$), a value of 0.018 N/m is obtained for $\Delta H_{d} = 24.1$ kJ/mol (M. Steiger, personal communication).

At low supersaturation, the nucleation rate of halite is large, while the nucleation of mirabilite requires a much higher supersaturation as expected from the high crystal−liquid interfacial energy.[7] Our own cooling experiments[17] show that epsomite is not prone to supersaturate, in agreement with Fig-

ure 1. For each salt, higher supersaturation initially enhances the nucleation rate according to the exponential dependence on $(\ln \beta)^2$ in eq 1. However, if supersaturation continues increasing, the high viscosity of the solution acts as an obstacle to nucleation and reduces the nucleation rate strongly. Thus, the high viscosity of a $MgSO_4$ solution[14] leads to the significant decrease of the nucleation rate with increasing concentration (Figure 1). Current ESEM studies of the crystallization of $MgSO_4$ salts from highly concentrated solution confirm this:[17] deliquescence of kieserite crystals was induced at 5 °C leading to the formation of a saturated solution with respect to kieserite and therefore strongly supersaturated with respect to epsomite ($\beta \approx 10.8$). By abrupt decrease of the RH, a rapid drying followed, which caused the droplet to dry and shrink, but no crystals were observed.

As water evaporates from the salt-bearing stone or masonry, the supersaturation of the pore solution increases until salt precipitates. A change of temperature, generally a decrease, may also lead to supersaturation of the solution, resulting in crystallization of salts. If evaporation occurs on the surface of the stone, then the crystals form a harmless (but unattractive) deposit on the surface called "efflorescence". However, if salts precipitate beneath the material surface (a phenomenon called subflorescence or cryptoflorescence), severe damage can result.

Whether efflorescence or subflorescence forms depends on the following factors:[18] (1) the drying rate, (2) the pore structure of the material,[19] and (3) surface tension and viscosity of the solution.[20] The rate of transport is strongly retarded by clogging of pores with salt crystals.[21] The intensity of pore clogging is strongly influenced by the type and amount of salt and by the pore structure of the substrate, but a better understanding of the salt−substrate interaction, as well as of the connection between pore-clogging and damage, must be developed so that these effects can be quantitatively predicted.

Crystallization pressure is the main reason for the damage caused by the crystallization of salts in a supersaturated solution.[3−5,7,8,10,22−25] Correns and Steinborn[23] (see also the annotated translation by Flatt et al.[26]) measured the growth pressure of a crystal against a load and derived an expression for the crystallization pressure as a function of the supersaturation ratio. They argued that the pressure depends on the existence of a thin layer of aqueous solution that remains between the crystal and pore wall, which permits diffusion of the ions to the growing crystal surface. If this thin layer of solution did not exist, the crystal would come into contact with the

pore wall, the growth would stop, and no crystallization pressure would be exerted, protecting the material from damage.[4,27]

The reason for the formation of a liquid film between the growing salt crystal and the pore surface is the action of repulsive forces (i.e., disjoining pressure). The repulsion may result from electrostatic interaction and structural forces, hydration forces being the most relevant structural forces in electrolyte solutions; the van der Waals forces are attractive at salt−mineral interfaces.[4,28]

Crystallization pressure, ΔP_C, must be exerted to maintain a crystal in equilibrium in a supersaturated solution:[5,10,24,25,29]

$$\Delta P_C = \frac{RT}{V_c} \ln \beta - \gamma_{cl}\kappa_{cl} + \frac{\Delta V}{V_c}\gamma_{lv}\kappa_{lv} \qquad (2)$$

where $\Delta V = \sum V_L - V_c$, $V_L = \sum V_i$ is the sum of ion molar volumes, V_c is the molar volume of crystal, κ_{cl} the curvature of the interface between crystal and solution, κ_{lv} is the curvature between liquid and vapor, γ_{cl} is the crystal−solution surface energy, and γ_{lv} is the vapor−solution surface energy. This concept can be applied to a crystal growing in a pore: the growth of the crystal is impeded by the pore wall, so the crystal remains in contact with a supersaturated solution, at least temporarily, and the pressure exerted by the crystal on the pore surface is given by eq 2. Once the supersaturation is consumed, crystallization pressure can no longer be exerted, which explains the transient course of the stress exerted on stone by salt.

The influence of the crystal curvature, given by the second term in eq 2, on the crystallization pressure must be considered in pores smaller than ∼0.1 μm. The maximal pressure occurs when a large crystal grows in a large pore (curvature κ_2) with small entries (κ_1):[6]

$$\Delta P_C^\infty = \gamma_{cl}(\kappa_1 - \kappa_2) \qquad (3)$$

If the material contains such pores, a static crystallization pressure can be expected if supersaturation exists but is not sufficient to permit a crystal to grow out of a large pore through its small entries.[5,25] Therefore porous materials with a bimodal pore size distribution, where one of the maxima consists of pores with radii smaller than ∼0.1 μm, are more sensitive to damage by crystallization pressure.

The action of the capillary pressure in unsaturated porous materials can be beneficial or prejudicial depending on the sign of ΔV in eq 2. For example, during the drying-induced crystallization of thenardite in limestone, negative capillary pressure leads to an increase of the crystallization pressure, because ΔV is negative.[30]

In a nonequilibrium state, even in the absence of small pores, high mechanical stresses may arise due to high supersaturation ratios, according to the first term in eq 2. That is, crystals grow against the pore walls, while the solution is highly supersaturated, and they exert force on the wall until equilibrium is established. At equilibrium, pores are filled with a saturated solution and stress-free crystals.

Understanding of in-pore nucleation and crystal growth rates suggests methods to prevent damage by salt crystallization. Thus, recent research has explored the use of additives to alter nucleation, crystal growth, solution properties, or disjoining pressure with the objective of reducing damage (see review in ref 11). Efficient treatments have been found for particular scenarios in the laboratory, such as nucleation promoters that reduce the threshold supersaturation for nucleation and thereby decrease crystallization pressure and damage. However, the consequences of these treatments in the field, such as the behavior at other temperatures and concentrations, as well as the application technique and durability of the treatments, are still the subject of current research.

Experimental Advances

The technological progress of recent years is providing new insights into the mechanism of in-pore crystallization from the nanometer to macroscopic scale, some of which are discussed here.

The ability of salt crystals to cause damage relies on a film of solution between the crystal and the pore surface that allows continued growth. The existence of this thin film has not yet been directly observed in salt crystallization experiments in porous materials. However, it has been experimentally proven by using NMR[31] and differential scanning calorimetry (DSC)[31,32] that when an ice crystal forms in a pore, an unfrozen water layer of a few nanometers remains between the ice crystal and the mineral surface due to repulsive van der Waals forces.[4] Thus, disjoining pressure is the cause for the formation of this thin film.

The disjoining pressure gives the upper bound for the crystallization pressure:[27] if the supersaturation is high enough to permit the crystallization pressure to exceed the disjoining pressure, the crystal is forced into contact with the pore wall, so growth stops and the pressure cannot increase further. If the disjoining pressure is smaller than the tensile strength of the material, in-pore crystallization cannot induce any damage to the material. Therefore it is of great interest to know the magnitude and nature of this force for each particular mineral−crystal system. Tabor and Winterton[33] and Israelachvili and Tabor[34] developed the first surface force apparatus

(SFA) for measuring interaction forces between molecularly smooth mica surfaces in air and vacuum. This sensitive technique can be used to measure electrostatic, van der Waals, and structural forces in aqueous solutions. There is currently much interest in developing alternative surfaces with different chemical and physical properties. Thus, the mica surface has been already used as a substrate for adsorbing or depositing a thin film of some other material. Materials other than mica have been utilized, such as sapphire[35] and silica,[36] both immersed in aqueous solution of NaCl.

The atomic force microscope (AFM) measures the interaction force between a fine tip and a surface. Ducker et al.[37] attached a micrometer-sized silica sphere to the end of an AFM tip and measured the long-range repulsive force between the sphere and a flat silica surface in aqueous NaCl solution; the forces were found to be similar to those obtained with the SFA, previously discussed. To date, no measurements of the surface forces between minerals and salt crystals have been conducted with AFM or SFA.

Ion transport within the solution film between crystal and pore surface determines the intensity and duration of the transient stress prior to reaching equilibrium. Thus, rapid ion diffusion permits a fast decrease of the supersaturation, allowing the crystal to continue growing on unstressed faces thus decreasing rapidly the crystallization pressure. On the contrary, hindered diffusion could be responsible for high and sustained stress.[7,30] Many studies of the structural and dynamic properties of water in different spatially restricted environments have been published in the past decade. The diffusive dynamics has been mostly studied by NMR,[38,40] quasi-elastic neutron scattering,[39] and beam bending,[40] which reveal a slowing of the motion of the confined water molecules compared with bulk water within a few angstroms of the pore wall. NMR is also a potential experimental technique to provide information about ion diffusion in confined geometries of nanometer size.

Environmental scanning electron microscopy (ESEM) provides visual information about the transitional states and kinetics of the phase changes of salts in situ. Rodriguez-Navarro and Doehne[3] showed that damage due to crystallization of mirabilite in a porous stone is strongly dependent on the environmental conditions that control its crystal habit, morphology, and growth rate. High supersaturation, due to more rapid evaporation at low relative humidity (RH), results in anhedral (nonequilibrium) crystal morphologies that cause significant damage, as macroscopic experiments under the same conditions showed. Other ESEM experiments show that the hydration path of thenardite into mirabilite at high RH is a
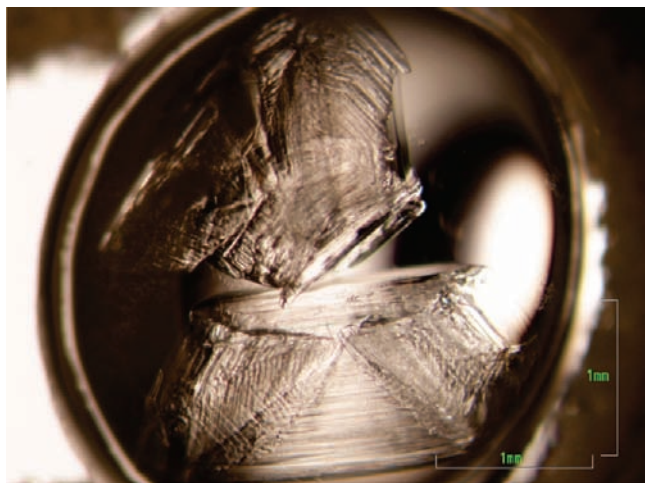
FIGURE 2. Image of sodium sulfate heptahydrate crystals precipitated in a 2.8 *m* sodium sulfate solution at 5 °C (photo courtesy of H. Derluyn).

through-dissolution process.[22] This confirms that when rain or groundwater penetrates into a (dry) thenardite-bearing stone, damage results from the action of the crystallization pressure exerted by the mirabilite crystals and not from a hydration pressure.

The damaging nature of salt crystallization is strongly determined by the ability of salts to achieve high supersaturation ratios, which is related to the liquid−crystal interfacial energy, and molecular volume. The formation of thermodynamically metastable salts has important consequences from the point of view of understanding salt weathering, since they have a higher solubility (e.g. sodium sulfate heptahydrate[42] or hexahydrite[17]) and therefore less ability to exert high stresses.

Differential scanning calorimetry (DSC) has been successfully applied to determine the threshold supersaturation for nucleation of stable and metastable sodium sulfate salts, as well as the crystallization rate in bulk solution and in the pores of limestones in cooling experiments.[7] Similar results were obtained using NMR[9,13] by direct measurement of the average concentration of the solution. It has been proven that during cooling the metastable sodium sulfate heptahydrate precipitates prior to mirabilite; mirabilite may precipitate below 0 °C. Figure 2 shows three heptahydrate crystals growing from a supersaturated solution (2.8 mol/kg) at 5 °C (i.e., at a supersaturation with respect to heptahydrate of 2.1).

X-ray diffraction (XRD) is an appropriate method to study kinetics of hydration, dehydration, deliquescence, and crystallization, by making measurements at controlled temperature and relative humidity to identify solid phases and determine crystal parameters. When applied to study phase transitions in porous stone, the drawback of this method is the fact that the spectra of salts and minerals are superimposed,

which reduces the sensitivity. However, hydration kinetics of Na_2SO_4[41] and $MgSO_4$[43] salts were successfully measured by XRD within the pores of porous glass frits, thus demonstrating the influence of a porous matrix on the transformation kinetics. The sensitivity problems in stone have been overcome by using hard synchrotron X-rays to obtain in situ powder diffraction patterns of salts within a porous mineral material during cooling experiments[9] and rewetting of thenardite.[44]

The close relation between supersaturation and crystallization pressure has been proven in cooling experiments[7] by using a dynamic mechanical analyzer to measure the deformation of limestone resulting from cooling-induced crystallization of sodium sulfate salts. Crystallization pressure and resulting stress in the stone can be determined using a thermoporoelastic model, discussed later. In drying experiments,[30] the crystallization pressure exerted by thenardite was determined by applying a model including transport and crystallization kinetics, along with poroelastic stress analysis.

Another novel method to determine crystallization pressure and stress is the warping experiment.[44] Here, the deflection of a stone−glass composite is measured during the rewetting of thenardite-bearing stone, which induces crystallization of mirabilite. The advantage of measuring deflection is that in-pore crystallization leads to a significant deflection of the composite without causing damage, which allows an elastic treatment of the mechanical problem. The warping test shows that drying-induced crystallization of thenardite puts the stone into tension. During rewetting, the stress release from thenardite dissolution and the superimposed expansion from the crystallization of mirabilite can be quantified at defined salt contents. Hence, the transformation of salts from lower to higher hydrated states, induced by rain, condensation, or rising damp, is a possible mechanism for salt weathering, even at low salt content. The resulting stress is strongly dependent on the permeability of the stone, which points to the dynamic nature of the salt weathering process.

Theoretical Advances in Modeling

Salt weathering is a strongly dynamic process, which is determined by the interaction of the kinetics of in-pore crystallization and dissolution, as well as other chemical reactions (e.g., dissolution of carbonate rocks[45,46]) with the transport of heat, moisture and salts through the pores under changing environmental conditions. In this section, we discuss how computer modeling helps us understand the complexity of these interacting processes.

In a continuum approach, the porous material is divided into elementary volumes where conservation of energy and mass of the porous matrix, gas, solution, and crystals is established. Currently available computational power permits simulations of these complex coupled processes (capillary flow, diffusion, evaporation, nucleation and growth of crystals, stress development) on both the laboratory and field scales (see review in ref 11).

From the point of view of comparing the behavior of different salts or porous materials or the effects of diverse climatic conditions, the development of such numerical models is of interest for practical applications. Since the kinetics of in-pore crystallization and the influence of pore clogging on transport are not completely understood, they cannot yet be modeled properly, and the applicability of the computational models is still restricted to specific scenarios. Progress on experimental work will be reflected in better models in the future.

Pore pressure induces deformation of the porous matrix. Biot's theory of poromechanics[47] has been classically used to determine the deformation and the stress caused by pore pressure in saturated and unsaturated materials. Recently, thermoporoelasticity has also been applied to freezing in concrete[48−50] and salt crystallization.[29,30]

If no external stress is applied to a porous material, it can be shown that crystallization pressure, ΔP_c, capillary pressure, Δp_L, temperature difference, ΔT, and dilatation, $\Delta \varepsilon$, are related by[29]

$$K\Delta\varepsilon - bS_C(\Delta P_c + \Delta p_L) - bS_L\Delta p_L - K\alpha\Delta T = 0 \qquad (4)$$

where K is the bulk modulus of the stone, α is the thermal dilatation coefficient, b is the Biot coefficient of the stone ($b = 1 - K/K_s$), K_s is the bulk modulus of the solid phase of the stone, and S_C and S_L are the saturations of (i.e., the volume fraction of the pores occupied by) precipitated salt crystals and liquid in the pores, respectively. Thus, if cooling-induced crystallization leads to a crystallization pressure of 12.5 MPa in a saturated limestone ($\Delta p_L = 0$) with $K = 10$ GPa, $b = 0.85$, $S_C = 0.5$, $S_L = 0.5$, $\Delta T = 10$ °C and $\alpha = 6$ μm/(m °C), the expected deformation is 471 μm/m. This is larger than the expected failure strain of any limestone, so damage should be expected. During drying or imbibition ($\Delta p_L \neq 0$), the deformation is coupled with the liquid flux and consequently deformation and liquid transport need to be analyzed together.[29,30,47]

The macroscopic stress is calculated by assuming a thermodynamically consistent overall elastic energy induced in the matrix by the pore pressure;[29,30,47] damage is predicted when a strain energy criterion is exceeded. A good estimate of the stress can be also obtained by multiplying the crystallization pressure by S_C.[9]

Each system has a maximum crystallization stress that is determined by the disjoining forces between salt and mineral in the liquid medium. A continuum approach can estimate the disjoining pressure by assuming that some of the bulk properties of the system are valid at the molecular level. Clearly, the applicability of this approach can be questioned, but it is still useful to give rough estimates or to understand the nature of measured forces.[28]

We consider a spherical quartz surface (1) and a flat KCl crystal (2) in saturated solution (3) at 25 °C. To estimate the van der Waals forces, the Lifshitz theory for the Hamaker constant A is used neglecting retardation effects. We obtain a positive $A = 6.9 \times 10^{-21}$ J with dielectric permeability[14,4] $\varepsilon_1 = 3.8$, $\varepsilon_2 = 4.86$, and $\varepsilon_3 = 78$, and refraction index[14,4] $n_1 = 1.44$, $n_2 = 1.4902$, and $n_3 = 1.333$. For the given geometry, the van der Waals force is

$$F_{vdW} = -\frac{AR_C}{6D^2} \qquad (5)$$

where D is the separation distance between crystal and pore surface and R_c is the crystal radius. Between salt crystal and mineral surface, F_{vdW} is attractive.

The electrostatic double-layer interaction, F_{EDL}, between charged surfaces (assuming the same electrical potential for surfaces 1 and 2) results from

$$F_{EDL} = -128\pi kTR_C\rho_\infty\gamma^2\kappa\,e^{-\kappa D} \qquad (6)$$

where ρ_∞ is the molecular density of solution, $1/\kappa$ is the Debye length for the diffuse electric layer, and γ is a function of the surface potential, ψ_0 (see eq 12.40 in ref 28). The Debye length is 1.38 Å for a 4.8 M KCl solution, which is a rough estimation due to the limitation of this theory to low ionic strength solutions. Values for the surface charge of silica in KCl solution can be found in the literature, and they increase with concentration from -0.15 C/m^2 at low concentrations up to -0.25 C/m^2 at 1 M.[51] In saturated solution, we assume a surface charge of KCl and of quartz equal to -0.3 C/m^2. By use of the Grahame equation (eq 12.30 in ref 28), ψ_0 is obtained, and the electrostatic force is calculated with eq 6. The resulting DLVO force ($F_{vdW} + F_{EDL}$) is repulsive below 0.4 nm, while AFM results show that the interaction between KCl and quartz is repulsive at a separation smaller than 4 nm[52] (Figure 3). The discrepancy between theory and experiment may arise because of the inaccuracy of EDL theory for high ionic strength solutions and because of non-DLVO forces, for example, due
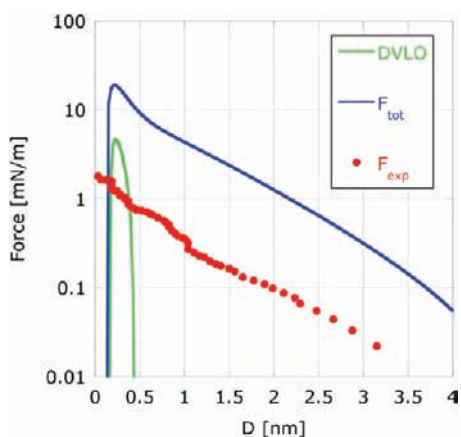
FIGURE 3. Estimated DVLO and total interaction force (on logarithmic scale) for the system quartz−potassium chloride compared with experimental results.[53]

to the presence of hydrated ions that disrupt the H-bonding network (hydration forces).[28]

Long-range hydration forces, F_{hyd}, are still poorly understood. Veeramasuneni et al.[52,53] show that the surface charge of a crystal resulting from ion−dipole interaction is influenced by the partial hydration of the ions at the surface, and this affects the hydration force. Thus, KCl has a negative surface charge, as does quartz, which leads to a repulsive interaction. In contrast, the surface charge of NaCl is positive, and consequently the force between NaCl and quartz is attractive.

An empirical exponential decay describes repulsive hydration force in terms of two empirical parameters, which were assumed here as $W_0 = 0.003$ and $\lambda_0 = 0.8 \times 10^{-9}$ according to ref 28. Figure 3 shows that the introduction of non-DLVO forces (F_{tot} = DVLO + F_{hyd}) leads to a repulsive resultant force between quartz and KCl crystals, qualitatively in agreement with experimental results (F_{exp}). Accordingly, potassium chloride can exert crystallization pressure on the pore wall of sandstone. However, more research is necessary to understand better and predict the action of the hydration forces.

A continuum approach has clear limitations at shorter distances. In contrast, a discrete approach, such as molecular dynamics (MD) or Monte Carlo simulation (MC), gives the correct solution providing the interaction potentials are known, which can only be established by comparing with experiments. MD predicts the trajectory of a molecule due to its interaction with the surrounding molecules, while MC only gives the equilibrium position. The required computational power is very high.

Many studies are focused on determining interaction potentials of molecules in confined geometry to determine the properties of the confined film.[40,54−56] Discrete models confirm that water close to the pore wall (≤1 nm) diffuses more slowly than bulk water in the middle of the pore.[40] MD simulations have also been performed to study the motion in an EDL showing that a very thin layer of fluid adheres to the surface and the mobility of the counterions decreases.[57] Simulations reveal a 2.0−2.5 nm interfacial region within which the self-diffusion coefficients of water and the electrolyte ions (Na$^+$, Cl$^-$) decrease significantly as the diffusing species approach the surface. Thus, both MD and experimental methods confirm the hindered mobility of the ions in the thin film between mineral and crystal. This would permit a gradient of concentration between the bulk pore solution and the thin film and explain the slow relaxation of the stress induced by the crystallization pressure.[7]

MD is currently being used to estimate the magnitude of the disjoining pressure in a system composed of NaCl, H$_2$O, and quartz, which shows that the net force is attractive,[58] in agreement with the previous discussion. Accordingly, halite cannot exert crystallization pressure in the pores of sandstone. Damage induced by halite in sandstone might be related to their significantly different thermal expansion coefficients, which may cause differential stresses. Moreover, impurities in the mineral or the solution, which are to be expected in the field, might reverse the interaction forces measured in pure systems. Since the interaction force depends also on the mineral properties, the resultant force between mineral and salt can be different in other rocks (e.g., carbonates).

Conclusions

This Account gives a state-of-the-art review of the knowledge of salt crystallization in porous materials. The theories of equilibrium and nonequilibrium thermodynamics and kinetics of crystallization and the concept of crystallization pressure were mostly developed in the 20th century and constitute the basic principles. New experimental methods are contributing to a better understanding of the phenomena involved in salt weathering. Increasing computational power permits numerical simulation of salt weathering processes from the molecular to the macroscopic scale. Continuum and discrete models can account for many of the remaining questions, particularly including the interaction between multiple phenomena.

We are still faced with several questions. How does nucleation and crystal growth take place within a pore network? How do the processes in the thin film affect the crystallization pressure? Does pore clogging enhance damage? Can we modify the disjoining pressure? Can we control nucleation and crystal growth in the field? Under what conditions does salt crystallization lead to crack propagation and failure of the material? Can we predict damage when salt mixtures or the

combined action of salt and swelling clays are involved? By understanding better the chemomechanics of in-pore salt crystallization, more reliable protection of monuments and sculptures against salt weathering will become possible.

BIOGRAPHICAL INFORMATION

Rosa M. Espinosa-Marzal received her Ph.D. in civil engineering in 2004 from TUHH, Germany. From 2004 to 2007, she was a postdoctoral researcher at TUHH. She joined Prof. Scherer's group as a postdoctoral fellow in 2007. Since September 2009, she has been a senior scientist in EMPA and a visiting scientist in the department of Surface Science and Technology at ETHZ. Her research involves the improvement of durability of building materials and the design of energetically, ecologically, and economically efficient construction materials.

George W. Scherer received his Ph.D. in materials science in 1974 from MIT. From 1974 to 1985, he worked at the research labs of the Corning Glass Works; then from 1985 through 1995, he was a member of the Central Research Department of the DuPont Company. He is the author of two books, ~250 papers, and 10 U.S. patents. He is a fellow of the American Ceramic Society and a member of the Materials Research Society. In 1997, he was elected to the National Academy of Engineering. In February, 1996, he became a full professor in the Department of Civil & Environmental Engineering at Princeton University, and a member of the Princeton Materials Institute (now called PRISM).

FOOTNOTES

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