Materials Science Research for the Conservation of Sculpture and Monuments

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Introduction

Mountains give the illusion of durability because their grand scale hides the continual weathering of their surfaces. When the same stone is used to create a sculpture, the loss of a few millimeters suffices to spoil, or even eliminate, the features of a face; the rate of loss may be surprising, but it is not necessarily unnatural. In this article, we review the causes of deterioration of sculpture and monuments made of stone and masonry, and examine various approaches to retarding or preventing the damage. Although our focus is on stone, we recognize that the same mechanisms of deterioration act in porous artifacts as diverse as pottery, porous pigments, frits, frescoes, and bone.[1]

Materials science has a central role to play in this field. The problem is particularly challenging because one has to treat an existing material, rather than create a more suitable one; moreover, one often has little or no control over the conditions of exposure. The goal of the conservation scientist is to diagnose the cause of the damage, then to choose and apply a treatment that will repair the damage and arrest the process of deterioration. There can be no generally applicable treatment for a given type of material because the damage reflects the microclimate to which the object is exposed, as well as its history (duration of exposure, previous repairs, etc.).

Unfortunately, the main causes of deterioration are only understood schematically. The details of the mechanisms that control the type of damage and the rate at which damage occurs are not clear. To provide accurate diagnosis and effective treatment, we must learn the fundamental mechanisms of deterioration. Table I outlines some of the phenomena that are of importance in stone* conservation and suggests some avenues for materials research. Although the list is long, it is obviously incomplete because it does not include decay related to biological agents or air pollution.

Since the field is vast, in this article we focus our attention on one important problem: the crystallization of salts. First, we examine in detail the mechanisms by which growing crystals do harm, and show how a clear understanding of the thermodynamics of the problem opens new avenues for treatment. We then consider two different approaches to conservation: *consolidants*, which are polymers or sol-gel materials that penetrate the damaged stone and bind its wounds, and *interfacial modification*, which includes treatments to prevent ingress of water and treatments that change the salt/stone interfacial energy in such a way as to prevent stress development. Finally, we outline areas in stone conservation where materials research is urgently needed. If this problem is neglected, the damage to our cultural heritage, whether natural or accelerated by inappropriate treatments, will continue to occur at an alarming rate.

*We occasionally use the word "stone" in this article as shorthand for porous materials including brick, concrete, and mortar.

Causes of Deterioration

Erosion and Corrosion

Erosion can be a problem for monuments in deserts or on sandy shores. The Sphinx is an interesting example. It was largely carved from bedrock, so it sits in a trough, and the sand carried by the wind mostly deposits in the trough, rather than striking the monument. However, there was a long period when the trough was filled with sand, so that the scouring wind directly struck the surface of the stone, and serious erosion occurred near what was then ground level.[2] For most monuments, particularly in urban environments, this kind of erosion is a minor problem. In contrast, corrosion by acidic rain is a major problem and is severely exacerbated by pollution; whereas ambient CO_2 can lower the pH of rain to ~5.6, oxides of sulfur and nitrogen from combustion of fossil fuels can reduce the pH to ~4. Winkler[3] shows a dramatic example, reproduced in Figure 1, in which a sculpture survived 206 years of exposure with minimal damage, but was so severely attacked by atmospheric pollution between 1908 and 1969 that all facial features were lost. Silicates are much less susceptible to corrosion than carbonates, but the latter include many of the most widely used stones in sculpture and architecture (e.g., marble, limestone, and calcareous sandstones, where the phase binding the grains is calcium carbonate).

Wetting and Drying

Cycles of wetting and drying can cause significant stresses because of the high capillary pressure in small pores. However, wetting is most destructive for stones that contain inclusions of swelling clay minerals. A spectacular example is a limestone used for carvings in Egypt that contains a large amount of sepiolite, a hydrous magnesium silicate, which causes the stone to expand by 3% when exposed to water.[4] A single wetting/drying cycle can destroy such a stone, and the artwork survived to our day only because it was in an arid environment. Less extreme cases of this phenomenon are abundant but underappreciated; in some cases where deterioration is blamed on salts or ice, the real culprit might be swelling of the clay.

Crystallization of Salts

Salts enter stone and masonry by several routes, the simplest of which is the capillary rise of groundwater.[5] As the water wicks up into a wall, it also evaporates

Table I: Scientific Questions Concerning Important Damage Mechanisms.

Phenomenon	Scientific Issue	Approach
Salt damage	Origin of supersaturation	Calculate driving force for nucleation and growth.
	Site of nucleation	Model evaporation, flow, diffusion, and precipitation.
	Effect of pore size distribution on stress	Model solute distribution in pore network.
	Role of interfacial energies	Molecular-dynamics study of salt/water/mineral interface; direct measurement of crystallization pressure.
Frost damage	Temperature of nucleation; degree of pore saturation	Field data (instrumentation of monuments).
	Relative importance of hydraulic pressure and crystallization pressure	Modeling of growth in pores; effect of saturation and pore size distribution.
Thermal stress	Magnitude of stress	Field data on temperature distribution in monuments; finite-element analysis of stresses in stone and masonry.
	Crack initiation and growth	Thermal-fatigue measurements.
	Effect of salts	Measure and model salt-containing samples.
	Effect of consolidants	Measure and model consolidated samples.
Wetting/drying damage	Role of clay inclusions	Relate measured dilatation to type and amount of clay; measure swelling potential of clays.
	Utility of passivation	Develop passivants for intercalation.
	Utility of consolidation	Measure effect of hydrophilic and hydrophobic consolidants on dilatation.
Consolidation	Adhesion to mineral surface; effect of weathering, salt deposits	Measure adhesion to single crystals before and after weathering.
	Distribution of consolidant in pores; control of cracking during drying	Model transport of consolidant, stress development during drying.
	Resistance to weathering; utility of hydrophobicity; utility of nonsilicate matrices	Test consolidants with particulate inclusions, nonsilicate matrices, hydrophobic, and/or biocidal surfaces.

from the free surface, as illustrated in Figure 2. Near the bottom of the wall (i.e., the source of the water), the flow through the pores is likely to be able to keep up with the rate of evaporation, so the liquid/vapor interface remains at the exterior surface. In that region, if the solution becomes supersaturated with salt, crystals will precipitate at the surface; this is called *efflorescence* (outward flowering),[6,7] and is responsible for the whitish stain often seen on new brick walls. Higher up the wall, the rate of capillary rise is slower, so that evaporation may dry out the surface and drive the liquid/vapor interface into the body. In that case, supersaturation leads to precipitation inside the pores, or *subflorescence*, which can cause damage. These internal crystals exert stress on the pore wall, as explained in detail in the section on "The Mechanics of Salt Crystallization Damage"; if the supersaturation of the solution is high, the stresses can exceed the tensile strength of stone (which is only a few megapascals).

Salt crystallization is one of the greatest threats to monuments in the Mediterranean basin. In that region, most of the salt is generated as an aerosol by the sea, then the particles are deposited on monuments by the wind. Rain dissolves the salt and allows it to wick into the stone; crystallization pressure is created when the water subsequently evaporates. Another sort of dry deposition mechanism is particularly important in polluted urban areas: oxides of sulfur react with calcium-bearing stone or cement to make gypsum ($CaSO_4 \cdot 2H_2O$). This salt is responsible for the black crust commonly seen on urban buildings. The black color comes from carbon particles generated from the burning of fossil fuels, which become incorporated into the gypsum. The crust may be smooth and hard, but it is not protective. A weakened zone of stone lies below it and will eventually lead to exfoliation.

Freeze/Thaw Cycles

Freezing and thawing cycles contribute to the formation of potholes in highways as well as cracking and spalling of artwork made of stone and masonry. Although it is widely thought that the damage results from the volume change as water converts to ice, a more important effect is the pressure exerted directly on the stone by the growing crystals. In fact, it has been shown that when water in a saturated porous glass is replaced by "normal" liquids (i.e., for which the solid phase is denser than the liquid), freezing causes similar expansion of the porous body.[8] The mechanism is the same as that by which salts do damage.

Thermal Stresses

Thermal stresses arise in a variety of ways and can contribute significantly to deterioration. Calcite, the form of calcium carbonate in marble and limestone, has an extremely anisotropic coefficient of thermal expansion (CTE) (+25 ppm/°C along the c axis and −6 ppm/°C along the a axis), so that polycrystalline bodies suffer internal stresses whenever the temperature changes; over a long period of time, that can lead to weakening of the body through development of microcracks.[9] If the pores of a stone become filled with salt, the mismatch in CTE, α, can be destructive; for example, $\alpha = 42$ ppm/°C for sodium chloride[10] and from 4 ppm to 12 ppm/°C for most kinds of stone.[11] Given that the thermal stress is roughly equal to the product $E\Delta\alpha\Delta T$, where the elastic modulus is $E \approx 35$ GPa, and the thermal-expansion mismatch between stone and salt is $\Delta\alpha \approx 30$ ppm/°C, the stress is about 1 MPa per degree change in temperature. Thus, the change in temperature from day to night could generate stresses exceeding the tensile strength of stone (<10 MPa),[12] if the pores were full of salt.

Mismatch in α between stone and mortar can also be problematic, particularly when the mortar is used to fill a crack in a

Figure 1. Example of erosion accelerated by atmospheric pollution. Statue carved in 1702 that was in excellent condition in a photo taken in 1908, but had lost all facial features by 1969. Reproduced by permission from Reference 3.

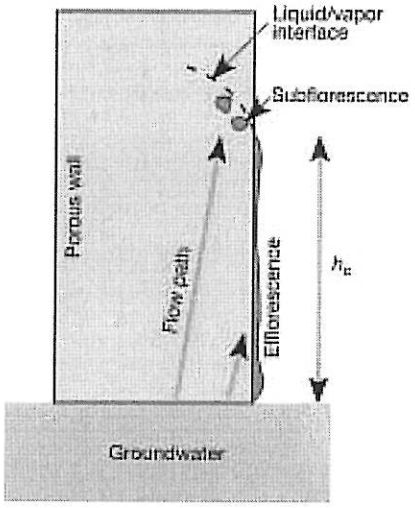

Figure 2. Schematic illustration of the capillary rise of groundwater into a wall, with simultaneous evaporation from the surface. Near the ground, the flow path is short, so the rate of rise more than matches the rate of evaporation, and the liquid/vapor interface is at the surface of the wall. The rate of rise decreases as the flow path becomes longer, and it becomes slower than the rate of evaporation beyond a certain height h_e. If evaporation causes the solution to become supersaturated, crystals precipitate at the exterior surface below h_e (efflorescence), but they precipitate within the wall above h_e (subflorescence).

stone.[13] Consolidants applied to reinforce a damaged stone can also cause thermal stresses because they are usually based on polymers or silica gel, which generally do not have the same expansion coefficient as the stone.

Biological Attack

Stone and masonry can be attacked by biota ranging from bacteria to algae to higher plants. Microorganisms cause damage by producing acidic secretions such as oxalic acid, whereas plants create mechanical stresses by sending roots into crevices. In some cases, biological growths seem to be completely benign, and some people feel that their presence improves the appearance of a monument. Other growths contribute indirectly to damage, by holding moisture at the surface of the stone and raising the risk of frost damage or corrosion. It is easiest for biota to take hold on a surface that is already weakened by some other mechanism of deterioration, so it is often difficult to distinguish the harm done by biota from that caused by other factors. Nevertheless, there are certainly cases where biota are principally responsible for significant damage.[14]

Damage from "Good Intentions"

A frustrating source of deterioration is a result of misguided attempts at repair. When confronted with a monument needing urgent intervention, the conservator must act immediately using the best tools available at the time. Unfortunately, the scientific basis for treatment is often inadequate, and the result of an inappropriate repair may be to accelerate the deterioration. Our aim is to acquire a detailed understanding of the mechanisms responsible for deterioration, so that we can provide the conservator with improved materials and methods for treatment. As an example, in the next two sections, we describe what is known about the mechanism of salt damage and outline strategies that are being developed for protection against such damage.

The Mechanism of Salt Crystallization Damage

Research on the pressure exerted by growing crystals began at least a century and a half ago,[15] when it was demonstrated that a crystal growing in a supersaturated solution could raise a weight placed upon it. The results were confirmed and extended early in the 20th century by geologists interested in the weathering of rocks by salt[16,17] (see Evans[18] for an excellent review of the role of salt in geological weathering). An important conclusion of this research was that there exists a film of liquid between a growing crystal and the adjacent surface: careful experiments showed that growth occurred on the bottom surface of the crystal, and the ions could not have attached themselves to that surface if there were not a film of liquid through which they could diffuse. Thus, a repulsive force must exist between the crystal and the surface of the container, and the force must act across the film of liquid.

For a crystal of ice, it is easy to see how such a film is sustained, because the van der Waals forces are repulsive between ice and most any other solid when a film of water lies between them. In general, if two materials with different refractive indices are separated by a third material whose index is intermediate, then the van der Waals interaction is repulsive.[19] Since the refractive index of ice is lower than that of water, whereas the indices of most minerals are higher, there is a repulsion between ice and stone;[20] electrostatic forces may enhance the repulsion. This phenomenon is responsible for frost heave, where soil particles are pushed upward by ice crystals growing underground.[21,22] In contrast to the case of ice

crystals, the van der Waals forces across a film of water separating a salt and a mineral surface are not repulsive. However, the electrostatic forces (from charged species on the surface and ions in the liquid) can be, and there may be some repulsion owing to the structure of the solvent adjacent to the interface. Molecular-dynamics modeling is needed to clarify these interactions.

The idea that ice typically repels minerals might seem surprising, since some mineral surfaces are capable of heterogeneously nucleating ice, so they must have certain crystallographic planes that have low interfacial energies with ice crystals. However, there is not usually more than one such plane in the structure, and that plane would not be expected to constitute the majority of the pore surface. For example, PbI_2 has a small lattice mismatch with ice on its basal plane, but not on other planes.[23] If one made a powder compact of PbI_2, the basal plane would be exposed at some points on the pore walls and could serve to nucleate ice; however, the adjacent grains would typically have an unfavorable orientation, so if the ice grew into contact with the opposite side of the pore or tried to spread laterally from its nucleation site, it would have to form higher-energy interfaces with those mineral surfaces. The same is true for crystals of salt that nucleate within porous bodies. If the energy of a new salt/mineral interface (γ_{sm}) would be greater than the sum of the energies of the existing salt/liquid (γ_{sl}) and mineral/liquid (γ_{ml}) interfaces, then work equal to $\gamma_{sm} - \gamma_{sl} - \gamma_{ml}$ must be done to force the surfaces into contact; this can constitute a large repulsive barrier.[24,25]

A crystal placed into a supersaturated solution tends to grow, but its growth can be prevented by applying a pressure p on its surface. The pressure required to stop growth is[24]

$$p = \left(\frac{R_g T}{V_m}\right) \ln\left(\frac{K}{K_0}\right), \quad (1)$$

where R_g is the gas constant, T is the absolute temperature, V_m is the molar volume of the crystal, and K and K_0 are the solubility products of the supersaturated and saturated solutions, respectively. For sodium chloride, $V_m = 24.55$ cm^3/mol, so if the solution were supersaturated by 10% ($K/K_0 = 1.1$) at 20°C, a pressure of 9.4 MPa would be required to prevent an existing crystal from growing. If the supersaturated solution exists within the pores of a stone, then the pore walls must exert pressure to suppress the growth of the crystal, and the necessary pressure may exceed the tensile strength of the stone.

Everett[26] was the first to point out that crystallization pressure is large only in small pores. For example, consider a crystal growing in a cylindrical pore, as in Figure 3. The pressure inside the hemispherical end of the crystal is given by Laplace's equation,

$$p = \left(\frac{2\gamma_{cl}}{r_p}\right), \quad (2)$$

where γ_{cl} is the crystal/liquid interfacial energy and r_p is the radius of the pore; the crystal is in equilibrium if the supersaturation satisfies Equation 1 with p replaced by Equation 2:

$$\frac{2\gamma_{cl}}{r_p} = \left(\frac{R_g T}{V_m}\right) \ln\left(\frac{K}{K_0}\right). \quad (3)$$

Since the sides of the crystal are cylindrical, the capillary contribution to the internal pressure on the cylindrical surface is only γ_{cl}/r_p, but that pressure cannot suppress growth in the presence of a supersaturation satisfying Equation 3. As the sides of the crystals try to grow (to achieve the equilibrium spheroidal shape), they are opposed by the pore walls. The pressure mounts until the crystal is forced into contact with the pore wall, or the total pressure on the sides becomes equal to that at the ends. In the latter case, the radial stress on the wall, σ_w, is equal to the difference between the capillary pressures on the ends and sides of the crystal:

$$\sigma_w = -\frac{\gamma_{cl}}{r_p}. \quad (4)$$

The negative sign indicates that the radial stress against the wall is compressive; however, the pressure generates *tensile* stress in the hoop direction that is of about equal magnitude.[20] Equation 4 shows that the crystallization pressure is significant only in small pores; if $\gamma_{cl} = 0.05$ J/m^2 (Reference 27), then the stress is 1 MPa if $r_p = 50$ nm, and 10 MPa if $r_p = 5$ nm.

The preceding calculation suggests that destructive stresses arise only in pores that are small compared with those in most stones, yet damage is sometimes seen in stone with relatively large pores, and is attributed to the presence of salt. That can be understood if we consider a case where the salt crystal is not in thermodynamic equilibrium. Suppose that a crystalline deposit has filled a large pore, as in Figure 4a; if the radius of the pore is large, then Equation 4 indicates that crystal growth cannot create large stresses. If the liquid evaporates, then the solution adjacent to the crystal increases in concentration, but it cannot exceed saturation because the crystal is free to grow in the pore and consume any supersaturation. However, if the liquid/vapor interface retreats into the gap between the crystal and the wall, as in Figure 4b, then the crystal is not in equilibrium; that is, there is no continuous film of liquid through which ions can move to equilibrate stresses. Once the continuous film is broken, the crystal cannot grow into the large pore entry; it can only grow in the region adjacent to the supersaturated solution where it is directly opposed by the wall. The pressure in that region will obey Equation 1 and can become very high (the exact expression[25] in-

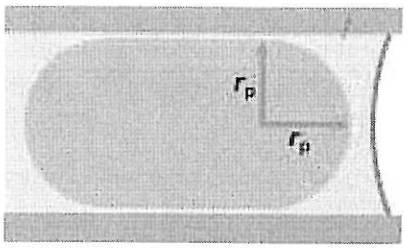

Figure 3. Crystal growing in a cylindrical pore with radius r_p has hemispherical ends whose curvature ($2/r_p$) is twice as great as that ($1/r_p$) of the cylindrical sides; the radial stress exerted by the crystal on the wall is proportional to the difference in curvature, $\sigma_w = -\gamma_{cl}/r_p$, where γ_{cl} is the crystal/liquid interfacial energy.

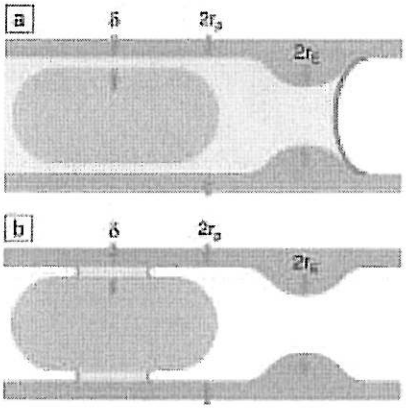

Figure 4. (a) A crystal in a large pore with radius r_p and entry radius r_E cannot generate high stresses at equilibrium; (b) when evaporation has driven the liquid into the gap (width δ) between the crystal and the pore wall, the sides of the crystal are no longer in equilibrium, and the stress is controlled only by the supersaturation and the interfacial repulsion.

volves interfacial curvatures, but we are assuming that the crystal is so large that those terms are negligible). The upper bound on the pressure is set by the repulsion between salt and stone: when that repulsion is overcome, the surfaces are forced into contact and growth stops; however, that stress is so great that fracture is likely to occur first.[25] Although we suspect that it is important, it has not yet been demonstrated that the mechanism in Figure 4b is responsible for the damage that is often seen in stone with large pores.

A crystal growing in a pore generates a stress field that is high near the pore wall, then dies away over a distance comparable to the pore size. Existing flaws in a stone can grow only if they lie within the stress field, so the stress in a small pore will only affect nearby small flaws. However, the flaws responsible for the low tensile strength of stone and masonry have lengths of the order of tens of micrometers, so crystallization pressures of a few megapascals will not cause those flaws to propagate unless the crystallized region extends over several micrometers. A stress field of that size could result from a large crystal under nonequilibrium conditions, as in Figure 4, or from crystals propagating through a network of small pores.[20] Thus, the susceptibility of a material to crystallization damage depends on the structure of the pore network, which controls the percolation of crystals, and not simply on the pore size. To date, the shape and intensity of the stress field, and the consequent initiation and propagation of cracks, have not been studied in depth.

Defending against Salt Damage

Environmental Control

Salts do not grow in the absence of water, so the most direct strategy for preventing salt damage is to control the environment of an object. Sometimes this is as simple as fixing the roof or sealing the foundation of a building, but moisture can also condense from the atmosphere, particularly when the relative humidity (RH) is suddenly raised by an influx of visitors or a sudden drop in temperature. An object in a museum can be stored under controlled humidity and temperature, but even then the appropriate conditions may require subtle analysis. Many salts exist as a variety of hydrates, depending on the temperature and humidity. For example, sodium sulfate exists as anhydrous thenardite, Na_2SO_4, or the decahydrate called mirabilite, $Na_2SO_4 \cdot 10H_2O$; above 35°C, only thenardite is stable, but at 20°C, mirabilite is stable at RH between about 94% and 75%. Thus, if the humidity rises above 75%, thenardite recrystallizes as mirabilite and can do serious damage. In the field, it is common to find a mixture of salts in a porous material, and there may be a very narrow range of humidity within which all phases are solid;[28] without detailed knowledge of the thermodynamics of the mixed salts, it is not possible to choose a safe range of RH for storage. One might think that museum pieces could simply be washed free of salt before display, but that is not always possible; some artifacts would crumble if the salt were removed, because the salt provides cohesion to the cracked object, and some artifacts contain swelling clays that make rewetting dangerous.

Waterproofing

If the source of water is external (e.g., rain, rather than rising groundwater), then a waterproofing treatment applied to the surface can be effective in preventing crystallization damage. Waterproofing or water-repellent treatments prevent liquid water from entering porous materials by changing the contact angle between water and the substrate to something greater than 90°. Most of these treatments are based on either silicone resins or polymeric perfluoro compounds.

However, if water invades from another direction, then salt crystals may grow under the hydrophobic layer; in temperate climates, water trapped under that layer may freeze. This can lead to catastrophic exfoliation of the treated layer.

Better methods are needed for tracing and quantifying the movement of water in porous media. This can be done with magnetic resonance imaging (MRI) in the laboratory[29] or with an array of sensors embedded in the wall of a monument.[30] Useful qualitative information can be obtained with infrared techniques,[31] but portable quantitative systems for use in the field are not available. If the path of the water can be traced, then treatments can be applied in the appropriate place.

Surface Modification

If the salt crystal were content to just touch the pore wall and not repel it, then growth would stop and stress would not develop. Therefore, it would be very helpful to develop a surface coating that could be applied to the internal surface of stone or masonry that would make the surface compatible with salt.[20] Certain polymers have a low interfacial energy with salt, but they do not make satisfactory protective coatings, because those polymers exhibit high osmotic swelling.[32] We speculate that a block copolymer could be designed with a segment that would adsorb on the stone (to prevent swelling) and another segment that would provide a low interfacial energy with salt. After treatment with such a material, salt could precipitate in the pores without generating stress; it would no longer be necessary to control the humidity or the ingress of water. Of course, if the salt fills the pores, then there could be a problem of thermal-expansion mismatch; in such cases, the coating would only be useful in an environment where the temperature is stable. The search for suitable coatings is an active area of research in our group.

Repair

Once damage has occurred, loose fragments and open fissures must be healed by using a *consolidant*. These are organic or inorganic polymeric materials with a low enough fluidity to permit them to penetrate to a depth of some centimeters into stone or masonry, where they harden and improve the mechanical properties of the stone. The properties of consolidants are examined in the next section.

Consolidants

An ideal consolidant should do the following things: (1) penetrate the pores of the material being treated to a depth of several centimeters, (2) bind chemically to the pore wall, (3) dry without cracking, (4) match the physical properties of the stone (CTE, elastic modulus), (5) leave the appearance unchanged, (6) arrest deterioration of the body, (7) restore strength, (8) control transportation of moisture, (9) control biological activity, and (10) provide reversibility (i.e., allow removal of the treatment without damage, so that superior treatments can be applied at a later date). Of course, no known consolidant does all of these things, and some do the opposite. For example, consolidants generally do not match the CTE of stone; fortunately, their moduli are usually so low that they cannot exert much stress on the stone in spite of the expansion mismatch. On the other hand, the low modulus makes them incapable of resisting expansion caused by salt in the pores or clay inclusions in the stone. Organic consolidants are sometimes found to be nutritious for destructive microbes, so applying them can be counterproductive.[33] A fundamental problem with consolidants is that they are not as strong as the original stone (except when the stone is extremely weak), so they will inevitably be destroyed by the same forces that damaged the stone. For that reason, we prefer to focus our research on ways of attacking directly the mechanisms of damage. However, where damage has occurred, there is a need for consolidation, so we must also consider ways of preparing optimal consolidants.

An obvious problem with most consolidants is that they are simple substances (silicate solutions or polymers), so there are not enough degrees of freedom in the formulation to allow many diverse requirements to be satisfied. Therefore, we have focused our research on composite inorganic systems; in particular, we are studying inorganic gel matrices with suspended colloidal particles of other oxides.[34–36] Reasonably inexpensive oxide particles of many kinds are available as unagglomerated submicron powders (for use as pigments or polishing compounds). The powders can be stabilized against aggregation by coating them with nanometric silica particles,[35] so that they form low-viscosity suspensions that readily penetrate stone. The presence of the particles reduces the shrinkage during drying, yielding nearly zero shrinkage for particle loadings above ~20 vol%. This means that the gels do not crack during drying and rewetting cycles, so their effectiveness as a binder is retained. By using a mixture of oxide particles, it is possible in principle to match a range of properties, such as color and CTE. The permeability of the consolidant is dependent on the size of the particulate inclusions,[35] so it can also be independently controlled.

Future Directions

There are serious gaps in our understanding of salt crystallization within porous materials. Outstanding questions include: (1) What are the nucleating heterogeneities, and how much supersaturation can develop before nucleation occurs? (2) Where do crystals nucleate and how do they propagate through the pore network? (3) What are the interfacial energies between various salts and minerals, and what can be done to modify them? (4) What is the nature and magnitude of the repulsive forces between salts and minerals? (5) What is the local distribution of stresses in a porous material as crystals grow? (6) How do cracks initiate and grow? (7) To what extent does thermal-expansion mismatch between stone and salt contribute to stress and cracking? (8) What is the mobility of water and ions in the gap between a salt crystal and mineral surface? Some of these questions can be addressed theoretically using molecular dynamics (e.g., 4) or finite element analysis (e.g., 5 and 7), and some (e.g., 2) can be addressed experimentally using techniques such as electron microscopy and MRI (which can now be applied to salts).[37]

Prevention of damage from crystallization pressure might be achieved with surface treatments that reduce the salt/stone interfacial energy, as mentioned earlier, but the principle has not yet been demonstrated. We are doing exploratory testing of a variety of monomeric and polymeric coating materials. Molecular-dynamics modeling will be used to examine the structure of the interface between salts and coatings, if promising candidates are identified. Other groups are using surfactants to modify or suppress the growth of crystals.[38]

Consolidants can be improved in several ways. Silica cannot bond chemically to carbonates, so coupling agents must be used to attach the consolidant to calcite. A variety of compounds, such as aminopropylsilane, have been examined;[39] a particularly promising approach is to modify the surface of the stone with tartaric acid, which creates a layer of hydroxyl groups to facilitate bonding.[40] Consolidants based on oxides other than silica, such as zirconates or titanates, might have advantages with respect to matching of properties; zirconates would be highly resistant to dissolution at high pH, which might be present if lime leaches from mortar into the adjacent stone or brick. We are exploring the use of submicron oxide particles as fillers in consolidants based on silica or other oxides[34–36] to permit control of mechanical, thermal, and optical properties. It may be necessary to make the mesoporous gel networks hydrophobic, so that they are not damaged by salt crystallization and/or to incorporate biocidal agents. Research is needed to determine how consolidants interact with salt deposits already present in the pores. Do salts cause premature gelation or alter the structure of the dried gel? Do salt deposits dissolve and leave voids within the consolidant, or do the deposits grow and crack the consolidant? If so, is it necessary to wash out the salt (which can be very difficult and possibly damaging), or can it be passivated with a coating prior to consolidation?

Surface treatments are also needed to protect stone against dissolution by acidic rain or biological agents. Chemical modification might also be effective in preventing the expansion of clays: intercalation of molecules that exclude water, or mechanically resist swelling, would protect many kinds of stone from damage during wetting/drying cycles.[41] Such passivating coatings would permit the washing out of salts and application of water-based consolidants to stones that would otherwise be damaged by the treatment itself.

Any treatment must be judged by its long-term effects, but one cannot wait a century for an evaluation. Therefore, it is essential to have reliable methods for accelerated testing, and that is not possible unless one understands the mechanisms responsible for damage. Otherwise, it is possible that the test will amplify the effect of a mechanism that is not important in the field. For example, stress created by the volume change of ice during freezing is greatest during rapid cooling, when crystals sweep rapidly through the pores; on the other hand, stress exerted directly on the pore walls by ice crystals is greatest at low temperatures (where the driving force for growth is high) and is sustained as long as the temperature remains low. Therefore, a test for frost damage that involves rapid cycling of temperature will exaggerate the susceptibility to the volume change (which might be appropriate for a monument in Manhattan), while a test using long dwells at low temperature will favor damage from crystallization pressure (appropriate for a monument in Quebec). One must use a test that reflects the field conditions to be experienced by the material of interest. Neither adequate tests nor effective interventions are possible unless one understands the details of the mechanisms by which damage is done.

Conclusions

Many important problems in the conservation of art fall within the scope of materials science, including understanding interfacial interactions and finding ways to modify them, analyzing complex patterns of growth in porous media and predicting the resulting stresses, developing improved materials for repair, and devising meaningful, accelerated testing methods. Relatively few materials scientists are engaged in this field of research. We encourage our colleagues to contribute to the search for methods for protecting our cultural heritage.

Acknowledgments

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