

## Chapter 5.2

# CONTROLLING STRESS FROM SALT CRYSTALLIZATION

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**Abstract:** Salt crystals are able to exert stress on the pore walls in stone because there is a repulsive force between the salt and mineral surfaces, so that a film of super-saturated solution is in contact with the growing crystal. Damage from salt could be prevented if the repulsion were eliminated, so we have screened a variety of organic systems to find species that adsorb on carbonates and on salts. Several candidates were identified and tested for their influence on nucleation and growth of sodium sulfate; promising systems were applied to Indiana limestone, which was then subjected to cycles of soaking in sodium sulfate solution followed by drying. The treatment that offered the most protection was polyacrylic acid with very low molecular weight.

**Key words:** crystallization pressure; nucleation; polymer; interfacial energy.

## 1. INTRODUCTION

Stresses created by crystallization of salts play an important role in the shaping of the natural environment<sup>1,2</sup>, as well as being a cause of deterioration of buildings, old and new. The goal of our research is to find a method for preventing damage to monuments from salt crystallization by attacking the cause: disjoining pressure. Salts normally repel minerals, so that growing crystals push the pore wall away and generate stress. If we could modify the surface of the stone so that the salt did not repel it, the salt crystal would grow into contact with the pore wall and stop, so there would be no stress or damage<sup>3</sup>. In this paper we present promising results for a water-based treatment that substantially reduces susceptibility of limestone to damage from sodium sulfate.

The origin of crystallization stress has been studied for more than a century, and the principles have recently been thoroughly reviewed<sup>4,5</sup>. It was

recognized by Becker and Day<sup>6</sup> and Taber<sup>7</sup> that the ability of a salt crystal to exert pressure on a confining surface indicates that a film of liquid is present between the two solids. Correns<sup>8</sup> argued that the two solids (viz., the growing salt and the confining mineral surface) resist contact if the energy of the new solid/solid interface exceeds the sum of the two solid/liquid interfaces. More generally, a crystal will repel the wall until the driving force for growth is so large that it can overcome the disjoining forces, which may result from van der Waals forces (for ice<sup>4</sup> and some organics<sup>9</sup>), electrostatic forces, or ordering of the solvent<sup>10</sup>. Only the latter two factors contribute to disjoining pressure for salts in stone, since the van der Waals forces between salts and minerals are attractive.

The pressure,  $p$ , that would have to be exerted on a salt crystal to prevent its growth is related to the supersaturation by<sup>5,8,11</sup>

$$p = \frac{R_g T}{V_C} \ln \left( \frac{Q}{K} \right) \quad (1)$$

where  $Q$  is the solubility product,  $K$  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. For a small crystal, the solubility product must exceed  $K$  by an amount that depends on its curvature,  $\kappa_{CL}$ , according to the Freundlich equation<sup>12</sup>

$$\gamma_{CL} \kappa_{CL} = \frac{R_g T}{V_C} \ln \left( \frac{Q}{K} \right) \quad (2)$$

where  $\gamma_{CL}$  is the crystal/liquid interfacial energy. For a polyhedral crystal with different surface energies,  $\gamma_i$ , for each face of type  $i$ , the Wulff condition<sup>13,14</sup> requires that the quantity  $\gamma_i/r_i$  be a constant, where  $r_i$  is the distance from the crystal face to the centroid. Therefore, for a polyhedral or spherical crystal, Eqs. (1) and (2) indicate that

$$p = \frac{2\gamma_{CL}}{r} \quad (3)$$

which implies that high crystallization pressures are only expected in small pores. Estimating the crystal/liquid interfacial energy of 0.1 J/m<sup>2</sup> for sodium sulfate<sup>15</sup>, Eq. (3) indicates that stresses exceeding 3 MPa would only be required to suppress growth of crystals smaller than ~70 nm. Since pores that small are relatively rare in stone, why is it so common to see damage caused by salt?

In fact, the pressure given by Eq. (1) is not the pressure exerted on the pore wall. If an irregular crystal (i.e., one having curvature that varies from

place to place) is surrounded by a solution, then equilibrium can exist only at points satisfying Eq.(2). In the case illustrated in Figure 1, the curvature of the portion of the crystal labeled E,  $\kappa_{CL}^E$ , is in equilibrium with the solution that surrounds the whole crystal, which has solubility product  $Q^E$ . At point C, where the curvature is less positive than at E, the equilibrium value for the solubility product would be  $Q^C < Q^E$ ; consequently, the crystal at P experiences a supersaturation of  $Q^C/Q^E$ , so it tends to grow and apply pressure on the pore wall equal to<sup>5</sup>

$$p_w = \kappa_{CL}^E - \kappa_{CL}^P = \frac{R_g T}{V_c} \ln \left( \frac{Q^E}{Q^P} \right) \quad (4)$$

If the interior of the pore is much larger than the pore entry, then  $\kappa_{CL}^C \rightarrow 0$  and  $Q^C \rightarrow K$ , so Eq.(4) reduces to Eq.(1), and the pressure is given by Eq.(3) with  $r$  equal to the radius of the pore entry.

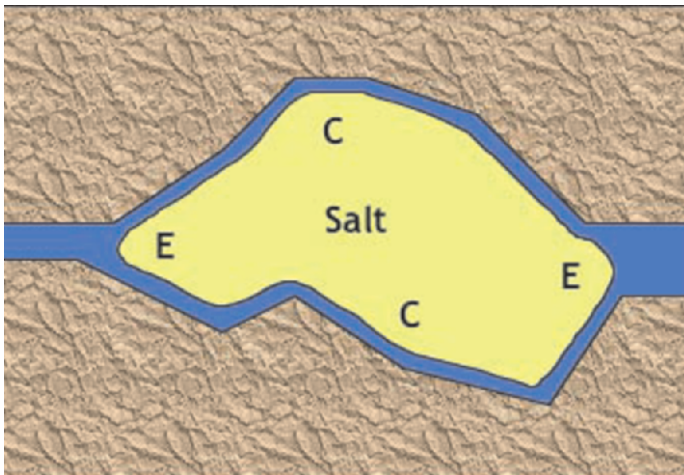
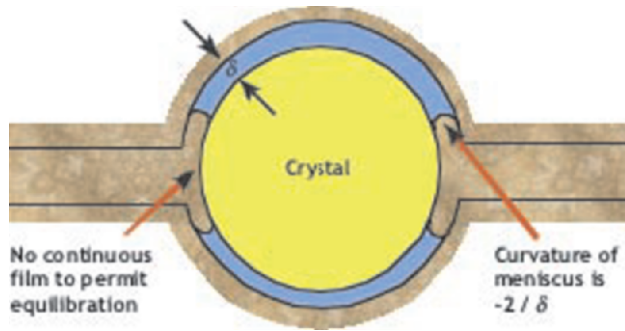


Figure 1. Crystal of salt in a large pore with small entries. The part of the salt crystal adjacent to the entry (at locations labeled “E”) has curvature in equilibrium with the solution that surrounds the crystal. At point C, the curvature is positive, but smaller than at E, so Eq.(2) is not satisfied and the crystal tends to grow, exerting pressure against the pore wall.

The preceding analysis indicates that high crystallization pressure only arises in small pores, but this conclusion is based on the assumption that the crystal is in equilibrium with a solution that bathes its entire surface. However, high pressures can develop in large pores, if the solution is only present as a film between the crystal and pore wall<sup>5,16</sup>, as in Figure 2. In that case, the supersaturation rises indefinitely as the liquid evaporates, and the crystal applies increasing pressure on the pore wall. The excess solute cannot be



*Figure 2.* As water evaporates from a porous body, isolated pockets of liquid can be trapped in clusters of pores with relatively small entries. As the liquid within those pockets evaporates, the solution may retreat into disconnected films lying between salt crystals and pore walls. In this sketch, a film of solution with thickness  $\delta$  is trapped between the crystal and the wall; as its concentration rises, the crystal applies increasing pressure on the wall.

consumed by growth in other directions, because the liquid does not extend around the surface. The upper bound on the pressure exerted on the pore wall is the disjoining pressure, which can amount to tens of megapascals<sup>16</sup>. The supersaturation is not related to the curvature of the crystal, so high stresses can be exerted by large crystals.

## 2. BACKGROUND

To avoid damaging crystallization pressure, it would be sufficient to eliminate the repulsive forces between the growing salt crystal and the pore wall<sup>3</sup>. This could be achieved by soaking stone with a solution that would alter the surface chemistry of the pores, so that it was attractive to salt. For example, certain polyelectrolytes are known to adsorb on carbonates and thereby inhibit their growth<sup>17</sup>. If the ligands that adsorb on the salt were attached to the pore wall, the wall might attract, rather than repel, the salt. For optimal interaction of the charged ligands with the surface of the salt, the spacing of the charges should be complementary. Therefore, coating the stone with a dense monolayer of ligands might be unfavorable, because they would not be likely to be properly spaced. However, if short polymers were attached to the wall, then they might have the necessary flexibility to adjust their spacings so as to interact with any ionic crystal that approached the wall. The optimal polymer would have a group capable of anchoring to the wall of the pore (e.g., carboxylic groups to attach to calcite) and a short chain with a ligand able to adsorb strongly onto various kinds of salt. If a salt crystal were to grow in a pore whose walls were covered with such a coating, the crystal would be attracted rather than repelled by the wall; it would grow into contact with the wall, but growth would then stop without any stress developing.

Following this idea, an early study<sup>18</sup> tested the effectiveness of polyacrylic acid (PAA) for protection against salt. An aqueous solution of the polymer was soaked into limestone, which was then exposed to cycles of soaking in sodium sulfate solution, then drying. The damage actually worsened compared to untreated stone, but the problem was the osmotic swelling of the polymer, which had too high a molecular weight, so that it filled the pores and generated more stress than the salt crystals. In the present study, we revisited this system using polymers of PAA with very low molecular weight, and obtained very positive results, as detailed below. Another polymer used in earlier tests<sup>19,20</sup> was a terpolymer (TP) containing ethylene, methacrylic acid, and isobutylacrylate groups. Unfortunately, TP is not soluble in water, and could only be dissolved in warm tetrahydrofuran. Limestone treated with this solution showed much improved resistance to sodium sulfate testing, but it was suspected that the difference resulted from reduced penetration of the salt solution into the stone, owing to the hydrophobic coating. In the present study, samples treated with TP were vacuum-saturated with the salt solution, so that there would be no ambiguity about the amount of salt present. On the basis of a survey of the literature regarding adsorption of organics on salts, a variety of other polymers were identified for testing.

Thomas et al.<sup>21</sup> found that fatty acids adsorbed to calcite nearly irreversibly, while carboxylated polymers and carboxylic acids bound less tightly and could be washed off, if the polymer was hydrophilic. These results suggest that fatty acids and hydrophobic (or mildly hydrophilic) carboxylic acids or carboxylated polymers are attractive candidates for surface modification of limestone. Polymers known to inhibit salt crystal and mineral growth include<sup>17,22-24</sup> phosphoric acid ( $-\text{OPO}(\text{OH})_2$ ), phosphonic acid ( $-\text{CPO}(\text{OH})_2$ ), and phenolic hydroxyl groups, as well as carboxylic acid ( $-\text{COOH}$ ). Inhibition is most efficient when polymers have a distribution of negatively charged functional groups spaced similarly to the distribution of cations of a growing crystal surface. Various factors affect the efficiency of crystallization inhibition: the relationship between the geometry of the polymer functional groups and the geometry of the mineral cations<sup>23-25</sup>; the quantity and rigidity of inhibitor functional groups as well as the molecular weight of the polymers<sup>17</sup>; the presence of non-inhibitor functional groups in the polymer (e.g.  $-\text{NH}_2$  and  $-\text{OH}$ ) that strengthen polymer adsorption by forming hydrogen bonding with crystal surface cations and water molecules in crystal hydrates<sup>22</sup>; and the pH of the mineral and polymer solutions, which can influence the amount of deprotonated functional groups along the polymer chain<sup>22</sup>. Sarig et al. conclude that polymers that are geometrically compatible with salts are the most effective crystal inhibitors of those salts, but Cody<sup>22</sup> notes that “very close crystal lattice fit cannot always be important, since the same organic substance is usually effective in modifying crystallization processes of a variety of minerals with different interatomic spacings.”

### 3. EXPERIMENTAL PROCEDURE

#### 3.1 Screening tests

On the basis of these previous studies, we selected the materials listed in Table 1 for further testing. Each of them is known to adsorb on calcite or to inhibit growth of calcite and/or gypsum. The organics were applied to Indiana Limestone (from Pasvalco, Closter, NJ) or single crystals of Iceland spar (Wards' Natural Science Establishment). The only salt used in the present study was sodium sulfate.

Table 1. Materials selected for study

Polymer	Manufacturer	CAS#	Functional Group	Density <sup>c</sup> (g/cm <sup>3</sup> )
Polyvinyl alcohol (99% hydrolyzed, ave MW 16000)	Acros organics	9002-89-5	Carboxylic acid	1.305
Maleic acid	Dajac Laboratories	110-16-7	Carboxylic acid	1.411
Acrylic acid (very low MW)	Dajac Laboratories	9003-01-04	Carboxylic acid	1.282
Acrylic acid (medium low MW)	Dajac Laboratories	9003-01-04	Carboxylic acid	
Xanthan gum	ICN Biomedical	11138-66-2	Carboxylic acid	
5-Phenylvaleric acid	Avocado Research Chemicals, Ltd.	2270-20-4	Carboxylic acid	1.218
Humic acid	Fluka Chemicals	1415-93-6	Carboxylic acid	1.581
Fumaric acid (99%)	Aldrich Chemical Co.	110-17-8	Carboxylic acid	1.624
TP <sup>a</sup>	DuPont		Carboxylic acid	0.947
Optima 100 <sup>b</sup>	Chryso, Inc		Diphosphate and ethylene oxide	1.059
1-Hexadecane sulfonic acid (Na salt, monohydrate, 99%)	Acros Organics	15015-81-3	Sulfonic acid	1.116

<sup>a</sup> Terpolymer with approximate composition ethylene (70 wt%), methacrylic acid (20 wt%), and isobutylacrylate (10 wt%); experimental polymer provided by Dr. John W. Paul of DuPont Packaging and Industrial Polymers. Based on the melt index (80 g/10 min), the molecular weight is estimated to be  $\sim 10^5$  g/mole.

<sup>b</sup> Optima 100 is a concrete superplasticizer that contains a diphosphate and ethylene oxide group.

<sup>c</sup> Measured by helium pycnometry (Accupyc 1330, Micromeritics).

To test the ability of the polymers to nucleate crystallization of the salt, samples of calcite were soaked in a solution containing 1.1 vol% of each polymer, then dried under cover (to prevent dust from settling on the sample). All of the solutions were prepared in water, except for TP, which had to be dissolved in tetrahydrofuran at 60 °C. The coated stone was then immersed in a solution of sodium sulfate saturated at room temperature, and the ensemble was placed in a cold stage (Physitemp TS-4) mounted under a Nikon SMZ-U zoom microscope, and cooled until nucleation was observed. Similar tests were made with a cup containing only the solution, and with a piece of calcite with no polymer coating. The tests were repeated three times for each case, but none showed any evidence of favoring nucleation compared to the solution alone (in which nucleation occurred at ~3 °C).

To evaluate the interaction between the organic coating and a growing salt crystal, a drop of solution was allowed to dry on the surface of a single crystal of calcite, then a drop of sodium sulfate solution was placed on the polymer and allowed to dry at room temperature. The contact angle of the solution was high on the samples treated with polyvinyl alcohol, hexadecane sulfonic acid and TP; the angle was intermediate on phenylvaleric acid, maleic acid, and medium molecular weight polyacrylic acid; the solution spread on Optima 100™, humic acid, and very low molecular weight polyacrylic acid (PAA-VLMW). In most cases, the crystals grew at the boundary of the droplet of solution; only on samples coated with humic acid or PAA-VLMW did the crystals spread across the surface of the polymer coating. The most striking and reproducible result was for PAA-VLMW, for which crystals with a unique morphology spread across the surface (see Figure 3). These crystals remain clear, so they are apparently thenardite ( $\text{Na}_2\text{SO}_4$ ), whereas mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) crystals turn white as they dehydrate.



Figure 3. Thenardite ( $\text{Na}_2\text{SO}_4$ ) crystals grown on the coating of PAA-VLMW on calcite.

### 3.2 Sulfate test

To test the influence of the organic coatings on the resistance of Indiana limestone to sulfate crystallization, two series of tests were performed. In the first two, five cubes (25 mm on each side) were soaked in each of the solutions, containing 1.1 vol% of the organic; xanthan gum and medium molecular weight polyacrylic acid were excluded, because the solutions were too viscous to penetrate the stone. The concentration was chosen so as to deposit about 1 nm of coating on the interior surface of the stone (surface area=0.7 m<sup>2</sup>/g, by BET analysis using nitrogen, ASAP 2010, Micromeritics). In each case, the stone was dried at 60 °C, then the solution (heated to the same temperature) was poured into a jar containing the stone until the sample was half submerged. Within an hour, the sample was saturated by capillary rise, so the excess solution was discarded and the stone was left in the oven to dry for at least 2 days. The elevated temperature was necessary for coating with TP, owing to its poor solubility; the same temperature was used for all solutions for the sake of consistency. During the application of the polymer, it was obvious that some of the organics were not suitable: 1-hexadecane sulfonic acid and fumaric acid reacted visibly with the limestone, and phenylvaleric acid produced a weight loss, while humic acid turned the stones dark brown. To insure that the stones were fully saturated with the salt solution, regardless of the effect of the organic treatment on the contact angle, vacuum saturation was employed. The samples were put individually into a desiccator, which was evacuated and then back-filled with a solution of sodium sulfate saturated at room temperature. Once the sample was covered with liquid, the atmosphere was admitted, so that the solution was driven into the sample by atmospheric pressure, in addition to capillary suction. The sample was allowed to soak for an hour before being placed in an open container, then transferred to an oven at 60 °C for drying.

In the first series of tests, the first two cycles of soaking and drying were performed at 60 °C, following the work of Tsui et al.<sup>26</sup>, which indicated that the growth of thenardite under these conditions would not cause damage. The advantage of the higher temperature is that more concentrated solutions can be used, so the pores of the stone are filled more quickly with salt. Subsequent cycles of soaking were done at room temperature with a solution saturated at that temperature (~22°C). Humic acid, hexadecane sulfonic acid, and polyvinyl alcohol all led to rapid deterioration relative to the untreated stone in the first tests, so they were not included in the next series. In the second series, all of the soaking cycles were performed at room temperature, and the samples were dried in a convection oven at 60°C for one day. The weight of a sample was found to stabilize after about 30 hours in the oven, as shown in Figure 4. Since some of the samples were removed after only 24 h, they might have retained as much as 5% of the original solution in liquid form. When samples were split in half after drying, slight efflorescence formed



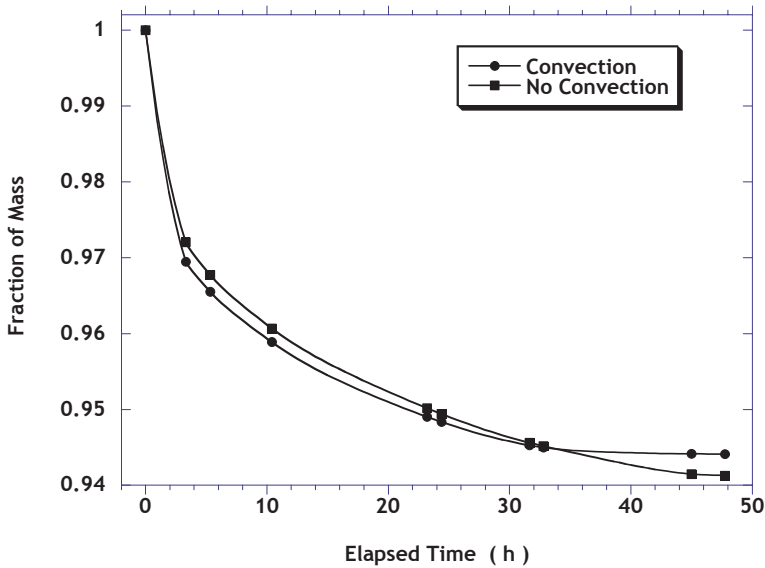


Figure 4. Weight versus time at 60 °C for stone sample in convection oven.

on the fracture surface, confirming the presence of some liquid in the pores. Incomplete drying compromises the results<sup>27</sup>, so future studies will employ more lengthy drying treatment.

Damage to the stone was evaluated by weighing the debris lost from each sample, collected from the individual containers in which they were dried. At the end of the series of cycles, representative cubes were split to reveal the distribution of salt inside.

## 4. RESULTS

The initial soaking at 60 °C succeeded in slightly raising the amount of salt in the samples of Series 1, as indicated in Figure 5. The additional salt may be responsible for the earlier loss of weight (at cycle 16) in Series 1.

Measurements of acoustic velocity (PUNDIT, 54 MHz) showed no significant change after application of the organic coatings, so no consolidation effect was produced. The only organic treatments that improved the resistance to the sulfate test were very low molecular weight polyacrylic acid (PAA-VLMW) or the terpolymer (TP). In the first series, TP was clearly superior, as shown in Figure 6, showing slow deterioration only after the untreated samples had collapsed. In this series, the PAA-VLMW samples suddenly failed after cycle 11, which coincided with resumption of the cycles after a pause of two weeks (during which the samples remained in the oven at 60 °C). It is possible that the sample had not dried completely in the previous cycles, and that the damage resulted from additional crystallization during the ex-

tended drying period. This seems unlikely, however, in view of the excellent performance of this polymer in the second series, shown in Figure 7. Treatment with maleic acid also provided some benefit in this series.

The physical appearance of the samples after cycle 16 in Series 2 is shown in Figure 8. The untreated stones are rounded owing to substantial damage on the faces and edges, while samples treated with PAA-VLMW show only minor damage on the edges.

After the 16<sup>th</sup> cycle in Series 2, several stones were split open to reveal the distribution of the salt. As shown in Figure 9, the salt was in a band just below the surface in the untreated stone and in the one treated with PAA-VLMW, as is typical for drying in a hydrophilic solid: evaporation removes

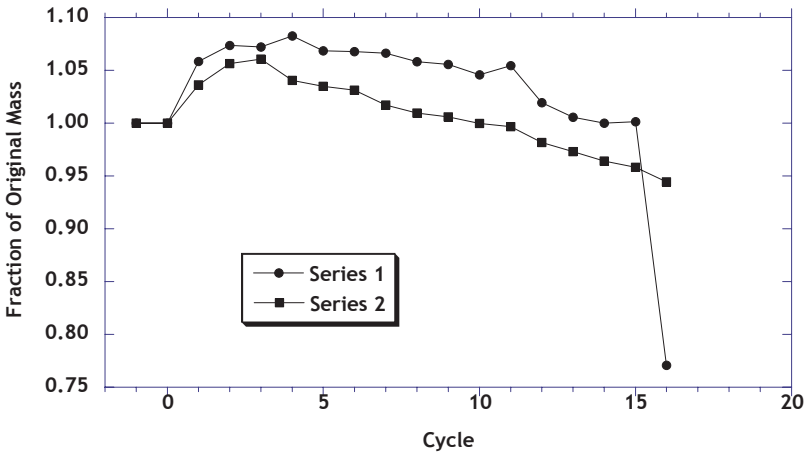


Figure 5. Average mass change for untreated stones in Series 1 and 2.

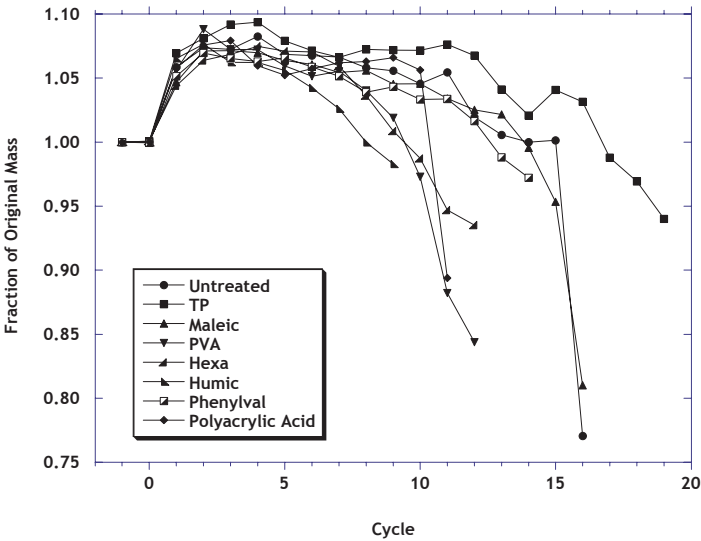


Figure 6. Average mass change of samples in Series 1.

liquid first from the larger pores, but capillary suction retains the solution in the smaller pores, preserving a contiguous network that allows the solution to flow toward the outer surface where it evaporates<sup>28</sup>. The salt accumulates in the location where evaporation occurs, so it appears near the surface in the stone treated with a hydrophilic polymer, such as PAA. The fact that the salt is concentrated at the surface, but causes less damage in the treated stone, is strong evidence that the polymer coating reduces the crystallization pressure. In contrast, the sample treated with the relatively hydrophobic TP had salt only in the center. This is to be expected when the contact angle approaches 90°, in which case there is not significant capillary pressure to draw the liquid toward the surface. Instead, it retreats into the interior and the salt accumulates there. This may mean that the protection provided by TP is illusory: the crystallization pressure is exerted only in the interior of the stone, where cracks are prevented from growing by confinement within the surrounding undamaged stone.

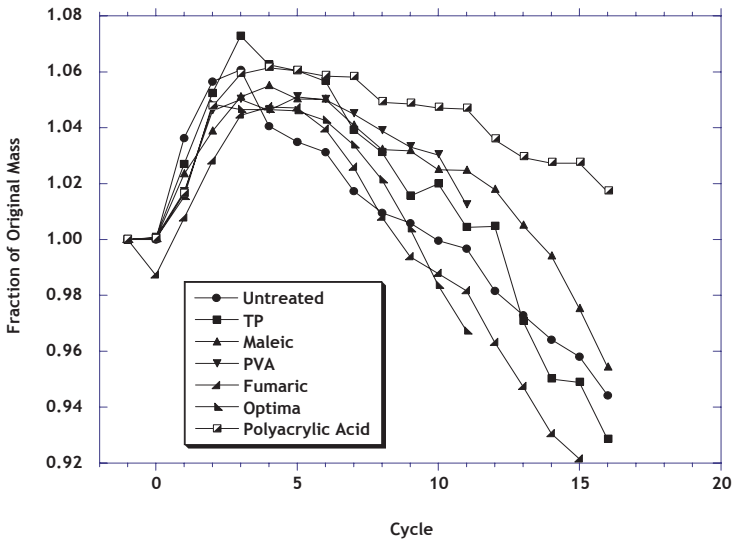


Figure 7. Average mass change of samples in Series 2.



Figure 8. Trial 2 Cycle 16: Untreated stones (left two) and stones treated with PAA-VLMW (right two). Untreated stones begin to round off while the treated stones show only slight deterioration at corners and edges.



Figure 9. Salt distribution in samples split open after cycle 16 in Series 2. Efflorescence appeared after 10-15 minutes, indicating location of salt. Untreated stone and sample treated with PAA-VLMW has ring of salt within ~1 mm of surface, whereas all salt has retreated to the center of the sample treated with the terpolymer.

## 5. CONCLUSIONS

Crystallization pressure can only be exerted on the pore walls when disjoining forces create a film of liquid between the crystal and the pore walls, which allows ions to attach to the growing surface. If the disjoining forces could be eliminated, then the crystal would grow into contact with the pore wall and growth would stop, so no pressure would be exerted. In this work, we identified several organic coatings with the potential to absorb on both salt and carbonate stone, and thereby reduce or eliminate disjoining forces between them. When a film of each coating was applied to a calcite crystal and exposed to a supersaturated solution of sodium sulfate, none of them showed enhanced ability to nucleate crystallization. This means that the distribution of charged sites in the organic layer was not initially similar to that in a crystal of sodium sulfate so that it could act as a substrate for heterogeneous nucleation. However, this does *not* mean that the layer of polymer could not adjust its structure to accommodate an existing crystal that approached the surface. That is, the polymers may not have the appropriate structure when no salt is present, but they have enough flexibility so that they could shift their charged sites into contact with those in an adjacent salt crystal when it approaches the coating.

When crystals were forced to grow on the polymers (by evaporation of a drop of solution), only polyacrylic acid clearly interacted with the crystals, inducing them to grow with a unique morphology along the coated surface. This polymer also provided substantial protection to the stone in Series 2 of the sodium sulfate tests, although it suddenly failed in Series 1 for reasons that are not clear. Another polymer that has shown promise in earlier tests, a relatively hydrophobic terpolymer, performed well in Series 1 of the sodium sulfate tests, but was less helpful in Series 2. The effectiveness of this polymer seems to be related to its effect on contact angle, rather than crystallization pressure, since it was found that the salt retreated to the interior of stones

coated with this polymer. In contrast, the salt accumulated near the outer surface of stones treated with PAA-VLMW, as it did in untreated stone. This implies that the PAA coating indeed reduced the crystallization pressure by reducing the disjoining forces between limestone and sodium sulfate. More detailed tests are underway to explore the potential of this treatment to protect limestone. Other anchoring groups and polymer architectures will also be explored, and wetting/drying cycles will be imposed to ascertain the durability of the polymer coatings.

For silicate stones, anchoring groups other than carboxylates will be necessary. The use of amine groups will be explored, since propylamine ligands seem to be effective at coupling silicate consolidants to stone<sup>29,30</sup>.

If one succeeds in making the surface of the pores attractive to salt, the possibility exists that the pore will fill with a dense volume of salt during repeated wetting/drying cycles. This could lead to significant stresses from thermal expansion mismatch between the stone and salt. The risk from this phenomenon will be evaluated through cycling tests (to monitor pore filling) and dilatometry (to evaluate thermal stress development).

## REFERENCES

1. I.S. Evans, Salt crystallization and rock weathering, *Rev. Géomorphologie dynamique* **XIX** (4) 153-177 (1969-70)
2. Goudie and H. Viles, *Salt Weathering Hazards* (Wiley, Chichester, 1997)
3. G.W. Scherer, R. Flatt, and G. Wheeler, Materials Science Research for Conservation of Sculpture and Monuments, *MRS Bulletin*, Jan. 2001, pp. 44-50
4. G.W. Scherer, Crystallization in pores, *Cement Concr. Res.* **29**(8) 1347-1358 (1999); Reply to discussion of Crystallization in pores, *Cement and Concr. Res.* **30**(4), 673-675 (2000)
5. G.W. Scherer, Stress from crystallization of salt, *Cement Concr. Res.* **34**, 1613-1624 (2004)
6. G.F. Becker and A.L. Day, Note on the linear force of growing crystals, *J. Geology* **XXIV**(4) 313-333 (1916)
7. S. Taber, The growth of crystals under external pressure, *Am. J. Sci.* **41**, 532-556 (1916)
8. C.W. Correns, Growth and dissolution of crystals under linear pressure, *Disc. Faraday Soc.* **5**, 267-271 (1949)
9. A.W. Neumann, S.N. Omenyi, and C.J. van Oss, Attraction and repulsion of solid particles by solidification fronts. 3. van der Waals interactions, *J. Phys. Chem.*, **86**, 1267-1270 (1982)
10. Israelachvili, *Intermolecular & Surface Forces*, 2nd ed. (Academic, London, 1992)
11. R.J. Flatt, Salt damage in porous materials: how high supersaturations are generated, *J. Cryst. Growth* **242**, 435-454 (2002)
12. J. Freundlich, *Colloid & Capillary Chemistry* (Methuen, London, 1926) pp. 154-157
13. G. Wulff, Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen (On the question of the growth and dissolution rates of crystalline faces), *Z. Krist.* **34**, 449-530 (1901)
14. A.W. Adamson, *Physical Chemistry of Surfaces*, 5th ed., (Wiley, New York, 1990)
15. L.A. Rijniers, Salt crystallization In porous materials: an NMR study, Ph.D. thesis, Technische Universiteit Eindhoven, Nov. 2004

16. G.W. Scherer, Stress from crystallization of salt in pores, pp. 187-194 in *Proc. 9th Int. Congress on Deterioration and Conservation of Stone*, Vol. 1, ed. V. Fassina (Elsevier, Amsterdam, 2000)
17. S. Sexmith and E.Q. Petrey, The use of polyelectrolytes for scale control in sea water evaporators, *Desalination* **13**, 87-90 (1973)
18. L. Gustafson, Polymer applications in stone: An attempt to decrease deterioration due to salt crystallization, Senior thesis, Dept. Chemical Eng., Princeton University, 1998
19. N. Alleyne, Art conservation: Testing interfacial energies, Senior thesis, Dept. Chemical Eng., Princeton University, 2001
20. L. Tangeman, The effects of polymer coatings in decreasing the interfacial energy between salt and stone, Senior thesis, Dept. Chemical Eng., Princeton University, 2002
21. M.M. Thomas, J.A. Couse, and J. Longo, Adsorption of organic compounds on carbonate minerals, *Chemical Geology*, **109**, 201-213 (1993)
22. R.D. Cody, Organo-crystalline interactions in evaporite systems: The effects of crystallization inhibition, *J. Sedimentary Petrology*, **65** (5) 704-715 (1990)
23. S. Sarig, A. Glasner, and J. Epstein, Crystal habit modifiers, *J. Crystal Growth*, **28**, 295-299 (1975)
24. S. Sarig and F. Kahana, On the association between sparingly soluble carbonates and polyelectrolytes, *J. Crystal Growth*, **35**, 145-152 (1976)
25. S. Sarig, F. Kahana, and R. Leshem, Selection of threshold agents for calcium sulfate scale control on the basis of chemical structure, *Desalination*, **17**, 215-229 (1975)
26. N. Tsui, R.J. Flatt, G.W. Scherer, Crystallization damage by sodium sulfate, *J. Cultural Heritage*, **4**, 109-115 (2003)
27. C.A. Price, The use of the sodium sulphate crystallisation test for determining the weathering resistance of untreated stone, in *Proc. UNESCO-RILEM Symposium on the Deterioration and Protection of Stone Monuments*, Vol. I. Sect. 3-6 (UNESCO/RILEM, Paris, 1978) pp. 1-24
28. G.W. Scherer, "Fundamentals of drying and shrinkage", in *Science of Whitewares*, eds. V.E. Henkes, G.Y. Onoda, and W.M. Carty (Am. Ceram. Soc., Westerville, OH, 1996) pp. 199-211
29. E. Wendler, D.D. Klemm, and R. Sneath, Consolidation and hydrophobic treatment of natural stone, in *Proc. 5th Int. Conference on Durability of Building Materials and Components*, eds. J.M. Baker, P.J. Nixon, A.J. Majumdar, and H. Davies (Chapman & Hall, London, 1991) pp. 203-212
30. K.L. Nagy, R.T. Cygan, C.S. Scotto, C.J. Brinker, and C.S. Ashley, Use of coupled passivants and consolidants on calcite mineral surfaces, in *Materials Issues in Art and Archaeology V* (Mater. Res. Soc., Pittsburgh, PA, 1997) pp. 301-306