DAMAGE TO MONUMENTS FROM THE CRYSTALLIZATION OF MIRABILITE, THENARDITE AND HALITE: MECHANISMS, ENVIRONMENT, AND PREVENTIVE POSSIBILITIES.

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Introduction: "In time, and with water, everything changes." ---Leonardo da Vinci

The crystallization of soluble salts in porous building materials is a widespread weathering process that results in damage to important monuments and archaeological sites [1]. Salt weathering by thenardite (sodium sulfate) and mirabilite (sodium sulfate decahydrate) is especially destructive, yet is still not fully understood [2]. Halite (sodium chloride) in contrast, is one of the least damaging salts [3]. Previous work has also demonstrated the importance of airflow in salt weathering [4]. Here we present new data that help explain why sodium sulfate is so damaging and also show how crystallization modifiers and changes in airflow can reduce salt damage in laboratory experiments.

Damage Mechanism: The behavior of sodium sulfate was documented using saturated solutions and oolites from Monks Park limestone (a stone well known to be vulnerable to salt damage) as test samples. Damage was evaluated based on the degree of cracking of the oolite. Observations of sodium sulfate behavior using the environmental scanning electron microscope (ESEM) and time-lapse video methods show that damage during wet/dry cycling generally only occurs after larger mirabilite crystals (~10 microns) undergo dehydration to thenardite, producing a high-surface area substrate of sub-micron crystals with strong capillary suction. When wetted, these thenardite crystals generally dissolve, rather than hydrate, resulting in extremely rapid crystallization, as observed in the ESEM. Simple crystallization and dissolution of mirabilite, without dehydration appears to cause little damage after 10 cycles.

Salt damage theory suggests that the limiting factor in causing damage is the need to sustain a solution *in situ* with a high supersaturation ratio [3]. This is generally difficult in many porous materials since their naturally rough surfaces tend to enhance crystallization once saturation is reached. Rapid cooling is one way to accomplish high supersaturation ratio in the sodium sulfate system. However, our *in situ* observations suggest that the process of cyclic dehydration followed by contact with a saturated solution of sodium sulfate can result in substantial damage to porous materials. Mitigation methods such as limiting the rapid cooling or rapid drying of porous, salt-laden stone through the use of shelters may reduce the damage potential of sodium sulfate.

Reducing Damage: Crystallization modifiers can significantly effect the capillary passage of dilute and concentrated solutions of sodium chloride and sodium sulfate through columns of limestone. The limestones were oolitic Monks Park stone where 90% of its pores measured between 0.05-0.80 microns and Texas Creme, a fossilferous stone with 90% of its pore size distribution measuring between 0.5 and 3.0 microns. In the absence of modifiers, sodium chloride passage through Monks Park limestone gave predominantly subflorescence with mild edge erosion while sodium sulfate mainly effloresced and severely damaged the stone column. With Texas Creme limestone, essentially only efflorescence occurred with either salt and there was little or no stone damage.

Most crystallization inhibitors--used in industry to prevent scaling by promoting high supersaturation levels for calcium compounds--plugged the columns or were otherwise without effect on the passage of salt solutions. Only alkali ferrocyanides were found to impact significantly on the interaction of these solutions as they moved through the limestone. The addition of 0.01-1.00% of $K_4Fe(CN)_6$ to sodium chloride in Monks Park limestone experiments increased the flow rate of solutions through the stone, resulting in slightly yellow-colored efflorescence in place of subflorescence, and yielded a massive formation of extended dendritic filaments without damaging the stone. This protection by additive was extended to sodium sulfate solutions, but only at lower salt concentrations. Results comparable to the effect of adding $K_4Fe(CN)_6$ to concentrated sodium chloride Monks Park limestone experiments were obtained with saturated sodium sulfate solutions without additives by conducting the experiments in a draft-free, high humidity environment--suggesting a potentially useful strategy for the conservation of fragile, salt-laden objects. These results are explained by factors causing evaporation of solution to occur either below or at the surface of the stone, and by the effect of modifiers on the crystal habit of the salts forming during evaporation in this region.

References:

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