ROLE OF CHEMICAL WEATHERING IN SALT DECAY OF ORNAMENTAL STONE

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INTRODUCTION

Salts are one of the main agents contributing to weathering of stone buildings. Mechanisms proposed to explain salt damage include: crystallization, hydration and osmotic pressure; mineral dissolution; and thermal expansion (Rodríguez-Navarro and Doehne, 1999). However, salt crystallization pressure within pores and cracks has been considered the main cause of salt damage to porous materials, neglecting the rest of the mechanisms. Moreover, most of the research conducted on stone weathering has studied chemical and physical phenomena as non-related mechanisms. Here we propose a general model for salt damage that combines both chemical and physical phenomena as a first step for effective conservation of cultural heritage.

RESULTS AND DISCUSSION

Limestone slabs were submitted to Na and Mg sulfate crystallization tests following the method outlined by Rodriguez-Navarro et al. (2002). Afterward, stone samples were observed with an environmental scanning electron microscope (ESEM). Additionally, pure calcite grains were immersed in saturated NaSO₄ and MgSO₄ solutions for 1, 2, 5, 7, 14, 21, 28 and 70 days, and observed by means of SEM. BET surface area of calcite was calculated from N₂ adsorption isotherms at 77 K.

After salt crystallization tests, calcite grains showed surface dissolution textures (figure 1). Formation of deep etch pits on calcite resulted in the development of microporosity. This was especially clear in the case of saturated MgSO₄ solution. In this case, the porosity increased the surface area of the calcite from 1.18 ± 0.01 m²g⁻¹ (aged calcite) to 2.72 ± 0.05 m²g⁻¹ (after 10 weeks in contact with saturated MgSO₄ solution). However, a reduction in surface area in the early stages was observed that could be due to the dissolution of the smaller particles. Formation of dissolution pits was observed in situ in the ESEM chamber after contact of Iceland spar crystals with saline solution. The initial calcite surfaces were perfectly flat and only growth steps were observed. After 1.5 h in contact with saturated NaSO₄ solution, dissolution features were observed at different scales. Sodium sulfate crystallization took place within such cracks and dissolution pits (figure 1). The repetition of salt crystallization–dissolution cycles resulted in the physical weathering of the stone.

![Figure 1: SEM photomicrograph of calcite grains showing etch pits filled with NaSO₄ crystals.](image)

Repeated cycles of crystallization and dissolution of salts in pores (both original pores of the stone or generated by mineral dissolution) lead to crack development and disintegration of the stone which in turn increases surface area and, therefore, the reactivity of the stone towards dissolution. New pores are thus generated and the process starts again, being a self-acceleratory process. This may explain why, in general, linear fits do not adjust well to weathering rates. In fact, such weathering vs. time data are best fitted to parabolic or even exponential functions. In conclusion, dissolution-induced porosity generation is a key factor to explaining salt damage either to non-porous stones such as marbles or granites and to stones with big pores that theoretically should not be highly affected by salt damage (in terms of crystallization pressure).

REFERENCES