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THE RESPONSE OF NaCl AND UMM ISHRIN SANDSTONE TO HUMIDITY CYCLING: MECHANISMS OF SALT WEATHERING

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Abstract

In order to better understand stone degradation due to salt weathering, a series of laboratory experiments were performed with NaCl, one of the most common salts in the field. Data from ESEM and optical microscopy experiments show that deliquescence and crystallization of NaCl are strongly influenced by the rate and magnitude of the humidity change, and to a lesser extent by the variations in crystal size.

The growth of salts in porous building materials can generate stress and provoke mechanical dilatation. Most stones respond to a relative humidity increase by expanding, while during drying they shrink. Dilatation measurements on Umm Ishrin sandstone from Petra, Jordan rapidly cycled under isothermal conditions from 30 to 92% RH, show this typical behaviour. However, when the same sandstone prisms are contaminated with sodium chloride results show that the presence of NaCl induces expansion during drying and contraction during humidity increase, with much higher amplitudes than the uncontaminated prisms. Flaking and granular disintegration were observed after only a few cycles, with dilatation amplitudes depending on the cycle duration. Overall, the cyclic expansion tended to exceed the contraction in amount and took place with a slower pace.

These experiments further illustrate mechanisms, parameters and underline the importance of NaCl-induced damage occurring in porous building materials.

Keywords: NaCl, Salt weathering, Dissolution/Crystallization, ESEM, Hygric Dilatation, Petra

1. Introduction

Salt weathering is a ubiquitous problem that takes place under a wide range of environmental conditions and affects rock outcrops, buildings, engineered structures and monuments. Its main impact is a loss of material through scaling, cracking, and granular disintegration in addition to aesthetic changes, such as efflorescence.

Several recent articles have reviewed this topic including Charola (2000) and Doehne (2002). It appears that damage from salts is a complex series of processes resulting from the intricate interaction of different parameters, including the properties of the substrate, the solution and the salts, and environmental parameters. Kinetic factors, such as the crystal growth and dissolution rate, also appear to play an important role.

Arnold & Zehnder (1988, 1991) have published several articles on the distribution of salts in porous media in the field. They point out the strong correlation between decay rates, the morphology of salt crystals, and the support moisture content. They observe that

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crystallization in the field is strongly influenced by relative humidity changes and for most salts to a lesser extent by temperature modifications.

The most important mechanism for salt damage appears to be crystallization pressure (Correns 1949). Nevertheless, although several theoretical models, extensive experimental and field data are reported in the literature, it is not yet clear what are the most important parameters which control the location and degree of damage (Charola & Weber 1992; Duttlinger & Knöfel 1993; Rodriguez-Navarro & Doehne 1999; Flatt 2002). Few kinetic studies have been performed (Doehne 2002), and while some studies show that 100 nm scale NaCl crystals deliquesce at lower RH than larger crystals, the dividing line for this behaviour is not well defined (Hameri 2001).

The aim of this paper is to further elucidate salt damage mechanisms. A series of dynamic experiments were performed by ESEM and optical microscopy in order to study the kinetics of NaCl on the micro-scale. On the macro-scale, NaCl-laden sandstone prisms were submitted to artificial weathering, by rapidly changing the relative humidity under isothermal conditions.

2. Methods and Instrumentation

2.1 Micro-experiment in a humidity-controlled box

Sodium chloride crystallization/dissolution experiments were recorded using a time-lapse system. Both crystals and micro-droplets of saturated solution lying on a glass plate were positioned inside a humidity-controlled box. Constant humidity was maintained by using specific saturated salt solutions: NaBr (RH_{eq} 59.1% at 20° C) during crystallization, and KNO_3 (RH_{eq} 94.6% at 20° C) during dissolution. RH was monitored inside the chamber. The experiment was continuously recorded using a CCD camera mounted on a stereomicroscope (Wild 420). Two cool white LED lamps (PLV 1005) were used for lighting the sample stage in order to keep any thermal effect of the light to a minimum. Experiments that last several hours in real time were condensed to a few minutes; providing a better match between information density, perception and the human visual system (Doehne 1994).

2.2 High magnification experiment in the ESEM

Dynamic crystallization experiments at high magnification were performed using an Environmental Scanning Electron Microscope (ESEM, FEI XL30/FEG). Observations in the micro-scale of dynamic process at high H_2O vapour pressure are possible in ESEM. RH conditions in the chamber are modified by an accurate control of temperature or pressure. In the present case, experiments were performed at constant temperature, using a Peltier stage, with variable pressure.

By introducing NaCl salt crystals or solution droplets on the Peltier stage and changing the relative humidity it has been possible to document the development of phenomena such as adsorption/desorption and dissolution/crystallization. Several time-lapse movies of these sequences were produced.

An important advantage of the ESEM with respect of the stereomicroscope set-up is a much more precise control of the RH, for instance at 10°C a 13 Pascal pressure variation corresponds to a 1% RH change. Since such pressure variation occurs immediately in the chamber, it is possible to simulate very precisely speed and magnitude of RH changes. Moreover, the behaviour of very small crystals (~ 2 μm) may be studied. Besides these advantages, ESEM experiments have one inconvenience in that water films are not transparent once they are more than a few microns thick. Indeed water molecules fixed on the crystal surface create an envelop through which it is impossible to see whether the remnants of the crystal are still present (adsorption and partial dissolution) or not (total dissolution).

2.3 Hygroscopic dilatation of NaCl-laden Umm Ishrin Sandstone under isothermal humidity cycling

The Nabataean site of Petra, Jordan has been the subject in the recent years of a systematic and thorough conservation approach within the Petra Stone Preservation project (Kühlenthal and Fischer 2000). Many among the rock-carved tomb facades are heavily contaminated with NaCl and endangered by consequent weathering processes (Heinrichs and Fitzner 2000). Most of the facades consist of Middle Umm Ishrin sandstone (Mid-Late Cambrian), which is medium to fine-grained, multi-coloured and composed of about 91% Quartz, 3% feldspar, 4% iron oxides and 2% minor accessories (Muscovite, Chlorite, Kaolinite, Illite) (Jaser and Bargous 1992).

Sandstone prisms were laden with NaCl by total immersion in saturated solution. After impregnation 5 faces of the prism were coated with latex to let the sample evaporate only from 1 face and lead to a salt profile comparable to those determined in situ with a significant enrichment at the surface for up to 10%. An uptake of 0.6% NaCl could be obtained for the bulk sandstone.

The hygroscopic dilatation was measured for uncontaminated and NaCl-laden Umm Ishrin sandstone prisms perpendicular to the layering at the surface. In order to simulate the weathering observed in the field, they were submitted to several rapid RH cycles (30-92%) under isothermal conditions (20° C) in a environmentally controlled chamber (Thermotron 2800). The cycle length is 48 hours with a rapid changing from wet to dry regime of 10-15 minutes. Five faces of the prism are covered by latex, allowing moisture exchange only from the surface of the prism. During the experiment the displacement (µm/m) of the stone, in response to the RH change, is continuously recorded by a electronic transducers positioned on the stone surface on an area free of latex (Fig. 1).

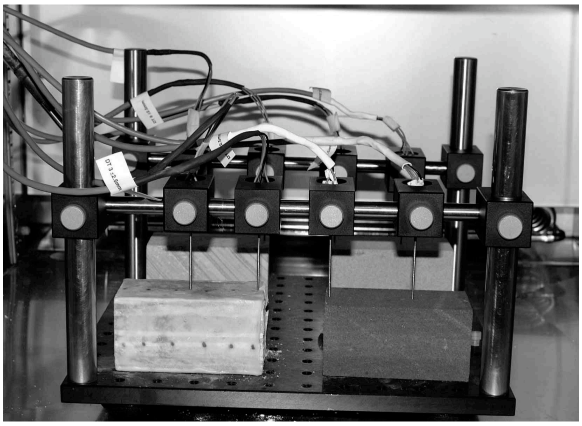


Fig. 1 Experimental set-up for hygroscopic dilatation measurement on fresh and salt-laden sandstone prisms in the isothermal humidity chamber.

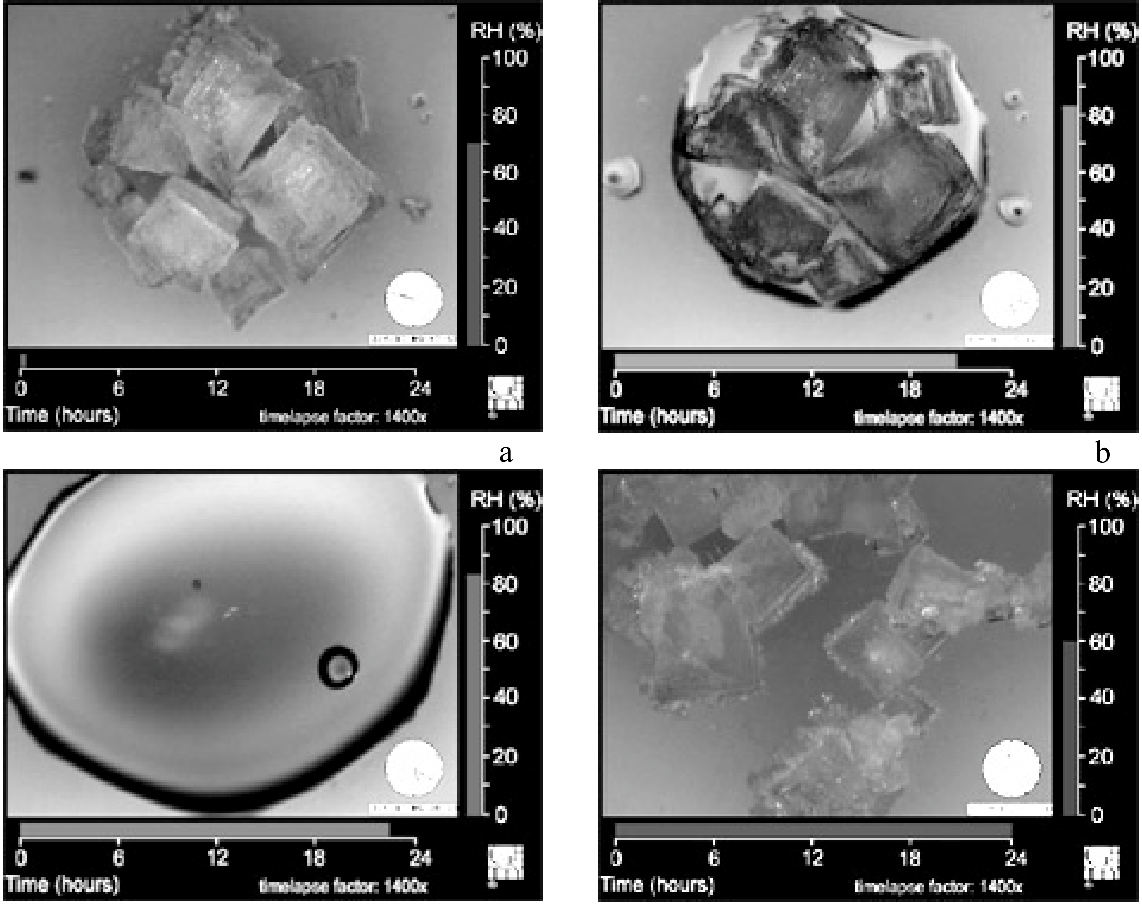
3. Results and Discussion

3.1 Dissolution/crystallization in a humidity-controlled box

Several experiment were performed as follows:

Dissolution / crystallization: Several crystals (0.9 – 2 mm) were submitted to ~80% RH. Adsorption of water vapor starts quickly; water envelops form around each crystal. As more water is fixed, crystals dissolve and solution droplets coalesceDissolution of crystals takes place in 20-25 hours (both small and large crystals have similar behavior at

80-89% RH); crystallization of saturated solutions at 50-60% RH in 3-7 hours. Towards the end of the crystallization cycle dendritic crystals often form.



a b

c d

Figure 1a-d: NaCl micro-crystals (a) submitted to high RH environment deliquesce (b) and dissolve after 20 hours (c). At 60% RH cubic crystals form in 4 hours, followed by smaller dendrite crystals (d).

3.2 High Magnification experiment in the ESEM

ESEM dynamic experiments were performed to elucidate the kinetics of NaCl crystallization. The investigated crystal sizes range from 100 to 500 µm. Results are summarized as follows:

Influence of crystal size in the adsorption/desorption (a/d) kinetics of NaCl: Crystals 100 and 250 µm in size were submitted to several RH cycles. Pressure was quickly raised up to 80% RH, as soon as the crystals disappeared under a water envelop, pressure was rapidly decreased to 70%, avoiding the full dissolution of the crystals. Results are summarized in table 2 (below).

These results confirm stereomicroscopy data:

While the experiments under the stereomicroscope showed dissolution of large crystals in an unconfined space being much slower than crystallisation, the adsorption of water vapour in the ESEM took place much faster than desorption. Nevertheless, crystals only become visible in the ESEM when the water film evaporates, while in the stereomicroscope they are visible as soon as they crystallize.

Table 2: ESEM dynamic experiments with NaCl crystals submitted to RH cycles (70›80›70 %).

	Crystal size : 100 µm		Crystal size : 250 µm	
Cycle	Adsorption	Desorption	Adsorption	Desorption
1	20 sec	200 sec	140 sec	420 sec
2	40 sec	360 sec	160 sec	480 sec
3	40 sec	330 sec	164 sec	480 sec
4	40 sec	360 sec	130 sec	480 sec

Influence of RH variation on the kinetics of NaCl crystallization: NaCl crystals were submitted to several RH cycles of varying amplitude and speed. The intermittent time between the changes was also varied. Results show that dissolution/crystallization are strongly influenced by the speed and the magnitude of the RH changes,

Small RH changes around the RHeq. (_RH ±2%), independent of the speed, and the amount of cycles, lead to reversible adsorption and desorption of water, and do not change the morphology of the crystals.

Slower speed RH changes (≥ 2 minutes) result in a partial dissolution when the magnitude of RH change is small (fig 2a,b) producing equilibrium crystals forms (cubic); and more extensive dissolution when the magnitude of the RH change is higher. In this case disequilibrium forms, such as prisms , may crystallize.

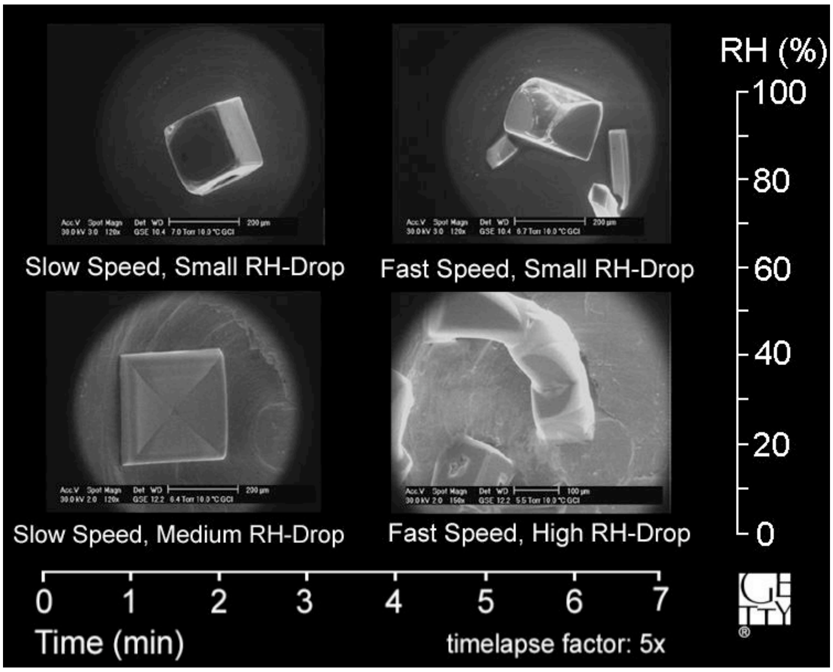


Figure 2: Dissolution/crystallization of NaCl crystals in ESEM. Fast crystallization results in different crystal forms than slow crystallization.

Rapid speed and high magnitude RH changes always result in extensive dissolution. Subsequently crystal morphology changes dramatically, and non-equilibrium crystal forms are observed (figure 2, lower right).

Rapid RH changes (few seconds) produce only a partial dissolution followed by reprecipitation if the magnitude of the RH change is small (RHeq<10%), ..

According to both stereomicroscope and ESEM experiments, it can be inferred that:

Cubic crystals appear as the equilibrium phase, while non-equilibrium phases (e.g. dendrite) often crystallize at the end of the crystallization cycle, as the solution surface/volume ratio changes.

Crystallization seems to take place more rapidly than dissolution, especially when the magnitude of RH change is large..

Crystal size and _RH are key factors in the kinetics of dissolution/crystallization of NaCl.. In the field, the presence of abundant nanometer size crystals is expected to result in a high crystallization pressure and produce significant damage.

The salt concentration of the solution seems to play a strong role in the crystallization kinetics of NaCl. Since salts in the field are usually concentrated on or near the surface of the object, crystallization is be facilitated, as a consequence of daily humidity cycles. In desert environments, such as Petra, where large RH changes are common, crystallization may occur rapidly and result in great damage

3.3 Hygroscopic dilatation of NaCl-laden Umm Ishrin Sandstone under isothermal humidity cycling

The mechanical dilatation response of fresh (salt-free) and NaCl laden Umm Ishrin sandstone is presented in fig. 5 for 8 subsequent climatic cycles. The fresh sandstone contracts during the drying phase and expands with increasing humidity RH. The dilatation movement occurs with constant speed and is completely reversible. Expansion and shrinkage mount to a similar magnitude of ~270 µm/m).

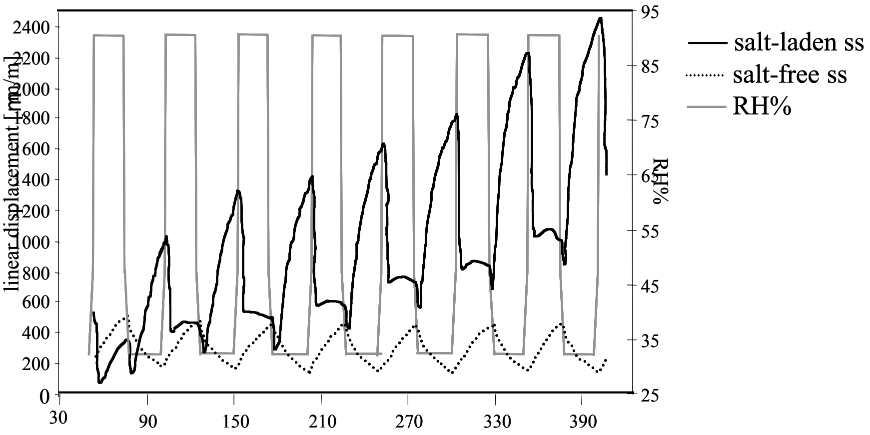


Figure 5: Dilatation (µm/m) as a function of time and _RH for fresh and salt-laden Umm Ishrin sandstone.

Two mechanisms of dilatation are competing in the salt-laden sandstone: It occurs in four steps:

a) During the dry phase (at 30% RH) expansion occurs due to the increasing crystallization of salt in the pore space. The movement looses speed with time, and doesn't reach the final value within the given 24 hours. With each cycle the dilatation increases from ca. 800 µm/m in the beginning to approx. 1600 µm/m at the end, reaching the dimension for hygric dilatation of clay rich sandstones.

b) During the wetting phase (from 30 to 92% RH) samples contract immediately due to the dissolution of the salt. The shrinkage proceeds faster than the expansion and is increasing as well over the subsequent cycles (~500 – 1200 µm/m). In contrary to the expansion, however the equilibrium values seem to be reached.

c) During the second half of the wet cycle a slight expansion can be recorded due to the presence of clay minerals in the stone. (> 50 µm/m)

d) After switching from the wet to the dry regime a short period of shrinkage is observed, also due to the content of expandable clay minerals, which takes place faster than their hygroscopic dilatation. It reaches a dimension of approx. 100-200 µm/m, before it is tied and overcome by the stronger dilation provoked by the crystallization of NaCl.

Fig..... Salt-laden sand stone prism in the dilatation measurement with developed surface flaking.

After only 10 humidity cycles substantial flaking could be observed on the exposed sandstone surface (Fig. 6)

According to the literature salt damage in a stone takes place when high solution supersaturations are reached (Rodriguez-Navarro & Doehne 1999). The driving force for the damage is usually rapid drying (NaCl), rapid temperature decrease ($NaSO_4$), or the presence of a highly soluble pre-existing phase during the impregnation phase (Doehne 2002; Flatt 2002). In the case of the Umm Ishrin sandstone the damage develops in the drying phase due to an irreversible and increasing expansion of the stone structure provoked by crystallization of NaCl. In very small pores a high solution supersaturation can be maintained for longer time and salt weathering may be more virulent. Once the damage is activated more small pores can form in the stone, crystallization at high supersaturation ratios is enhanced and expansion increases with the number of cycles.

4. Conclusion

Salt deterioration occurs as a result of subsequent phase transitions between aqueous solution and solid states, which are activated by changes of the environmental parameters. In the case of NaCl this transition occurs at the deliquescence point (75.5%, over a broad range independently on the temperature). Experiments performed by both ESEM and stereomicroscopy in RH controlled environment show that RH variation and speed is key factors in the kinetics of dissolution/crystallization of NaCl. Non-equilibrium forms appear preferentially as a result of high-magnitude, high-speed RH changes. These crystal forms correspond to higher supersaturation ratio in the solution and thus to higher crystallization pressure, which may result in greater damage. The effect of other variables on crystallization kinetics such as airflow and the temperature should be further investigated.

RH cycling of NaCl-laden Umm Ishrin sandstone, shows that repeated crystallization of salt inside the pore structure results in macro-scale damage similar to that observed in the field. Samples suffer loss of surface material by flaking and granular disintegration.

5. Acknowledgment

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