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Salt Weathering on Buildings and Stone Sculptures

Editors:
I. Ioannou & M. Theodoridou

EDITORS:

Ioannis Ioannou, PhD
University of Cyprus
Department of Civil and Environmental Engineering
Building Materials & Ledra Laboratories
PO Box 20537
1678 Nicosia
Cyprus
ioannis@ucy.ac.cy

Magdalini Theodoridou, PhD
University of Cyprus
Department of Civil and Environmental Engineering
Building Materials & Ledra Laboratories
PO Box 20537
1678 Nicosia
Cyprus
mtheodo@ucy.ac.cy

Dynamics of salt crystallization

Desarnaud J. [1][2], Bertrand F [1]., Shahidzadeh-Bonn N.[1*]

[1] Laboratoire Navier, Umr 8205, Marne la vallée, France
[2] Van der Waals-Zeeman Instituut, University of Amsterdam, Amsterdam, Netherlands
*corresponding author´s email: shahidzadeh.noushine@gmail.com

ABSTRACT

We study the impact of the recrystallization dynamics on damage of sandstone during wetting/drying and humidity cycling for NaCl and compare with the case of Na$_2$SO$_4$. These results reveal the major role of the crystallization dynamics in the way different salts cause damage under different environmental conditions. For sodium chloride, damage on Prague Sandstone is found to occur rather during humidity cycling than rewetting/ drying cycles. We show for the first time that deliquescence/recrystallization with humidity cycling leads to the growth of salt crystals by expulsing impurities in a process akin to the zone refining used in the semiconductor industry to obtain high-quality single crystals. The consequence of that is the faster growth of less nuclei with the progression of cycles leading to larger crystals and higher supersaturations before nucleation. This in turn leads to a higher crystallization pressure and hence more damage.

Keywords: sandstone, droplets, dissolution, deliquescence, recrystallization

1   INTRODUCTION

Crystallization is a very important subject in different fields of science and technology such as the purification of pharmaceuticals, the semiconductor industry, protein purification or for the prevention of salt damage to our cultural heritage. Any crystallization process consists of two major steps: crystal nucleation and growth. The rate of nucleation and the growth speed are driven by the supersaturation ($\Delta\mu$) of the solution, since the latter is the driving force of both processes :

$$\Delta\mu = \mu_s - \mu_c \approx kT \ln S \qquad (1)$$

where μ_s and μ_c are the chemical potentials of a molecule in solution and in the bulk of the crystal phase, respectively; k is the Boltzmann constant, T is the absolute temperature and S is the relative supersaturation defined as (S=C/C$_{sat}$). Due to the fact that in practice, nucleation is heterogeneous, the size, shape and crystalline order are in general limited by a combination of thermodynamic and kinetic parameters (Steiger & Asmussen 2008; Shahidzadeh-Bonn et al. 2010, 2008 ; Boistelle & Astier 1988).

In the field of building conservation it is well known that repeated cycles of dissolution-crystallization of salts that are present in the stones (due to wetting by rain, capillary rise or humidity variations followed by drying) can provoke severe damage of building materials (Shahidzadeh-Bonn et al. 2010; Espinosa-Marzal & Scherer 2008; Steiger 2005; Scherer 2004, Lubelli et al. 2004, Flatt 2002). The detailed mechanisms of the damaging processes have been

investigated for several decades now. Different theoretical explanations have been proposed; currently the most popular ones to explain the damage are either the crystallization pressure against the pore walls (which is proportional to the degree of supersaturation) (Steiger 2005, Scherer 2004; Flatt 2002) or volume variations in the salt structure during wetting and drying cycles (Goudies & Viles 1997). Although the existence of a supersaturation can account for an excess pressure exerted by the salt crystals against the pore walls and hence the damage, there are still many open questions on the mechanisms that cause salt damage. Notably, it is unclear why the same salt is damaging under some experimental conditions but not in others. For the case of NaCl, different and at first sight contradictory results have been reported in the literature. Some authors reported irreversible dilation of salt-containing stone leading to flaking and granular disintegration (Lubelli et al. 2006; Lombardo et al 2004) with humidity cycling, whereas others report hardly any damage during rewetting/crystallization cycles with liquid water (Shahidzadeh-Bonn et al. 2010; Pel et al. 2002). Consequently, a detailed understanding of how crystal growth within the porous media leads to damage still remains elusive. The experiments reported here shed some light on this issue.

The objective of our study was to elucidate to what extent the dynamics of crystallization is important in the damaging process. For this purpose we have investigated how dissolution/ crystallization and deliquescence/ crystallization provokes stone degradation and under what conditions. There are in general two ways in which salts, once crystallized, can take up water again: by bringing it in contact with liquid water (dissolution) or with water vapor (deliquescence). Because of the hygroscopic properties of salts, deliquescence will occur when the RH (relative humidity) is higher than the RH_{eq} of the salt solution (75% at 21°C for NaCl). Our results reported in this paper show for the first time that deliquescence allows to expel impurities from crystals and obtain pure NaCl single crystals easily during moderate to slow drying (Relative Humidity RH~50%). The solutions can reach high supersaturations before the nucleation and subsequent crystal growth. As a consequence, a smaller number of larger crystals is obtained with the progression of cycles. The comparison of these results with the situation in which recrystallization is provoked after dissolution with liquid water demonstrates for the first time how the kinetics of crystallization and the interfacial properties of the salt solutions and crystals at microscopic scale can explain the damage observed at macroscopic scale.

2   EXPERIMENTAL SECTION

 We performed experiments on sodium chloride crystallization both at macroscopic and microscopic scales. Sodium chloride is known to have only one stable anhydrous phase (cubic) at room temperature. Saturated sodium chloride solutions (26.4% wt or 6.1M) are prepared with NaCl (Sigma Aldrich grade).

The macroscale experiments consist of studying the behavior of salt contaminated sandstones (obtained by one cycle of impregnation and drying with saturated salt solution; C1 for first cycle) once rewetted with liquid water or water vapor (for the latter case the sample is put in an environment of RH~ 100%) followed by drying at constant environmental conditions (T=21°C and RH~48%).

The sandstone used in this study is a Mesne sandstone with a porosity ϕ~29%, and pore diameter $d_p = 30$ μm. The weight of stones is followed in time during drying on an automated balance with a precision of (± 0.001 g). Proton MRI was used to follow the saturation profiles during water uptake and drying cycles; experiments were performed on a vertical Bruker Spectrometer with a field strength of 0.5T and 1d spin echo sequence,.

At the microscopic scale, using phase contrast microscopy and direct imaging we investigate the kinetics of dissolution of crystals in contact with liquid water and also their deliquescence in contact with water vapor, followed by recrystallization during the evaporation. Experiments

were done in unconfined (droplet evaporation of different volume drops 0.1, 2, 5 μl) or confined geometries (square microcapillaries of different sizes 50, 100 μm) with different wetting properties (hydrophilic and hydrophobic) to investigate the generality of the results obtained.

3   RESULTS

3.1.   *Macroscopic experiments*

During a first cycle (C1), the sandstone samples were saturated by imbibition with saturated salt solutions (26.4 wt% for NaCl) and left to dry. At the end of drying, the amount of salt crystallized at the surface as efflorescence that can be gently removed with a toothbrush is around ~20%±2. The efflorescence strongly adheres to the sandstone. No damage to the stone (loss of materials) is observed at this step. Salt contaminated stones (80% of the salt as subflorescence, i.e., in the stone), are subsequently saturated either with pure water by imbibition or by bringing them in contact with saturated water vapor.

Our observations are the following. The rewetting by imbibition of the sample is a very rapid process, taking less than 2 minutes, whereas the complete saturation in contact with water vapor can take 10 days in our samples of dimension 2x2x2.5 cm. The saturation profiles obtained by MRI show a very homogeneous water uptake of the salt contaminated sandstone in contact water vapor (figure 1).
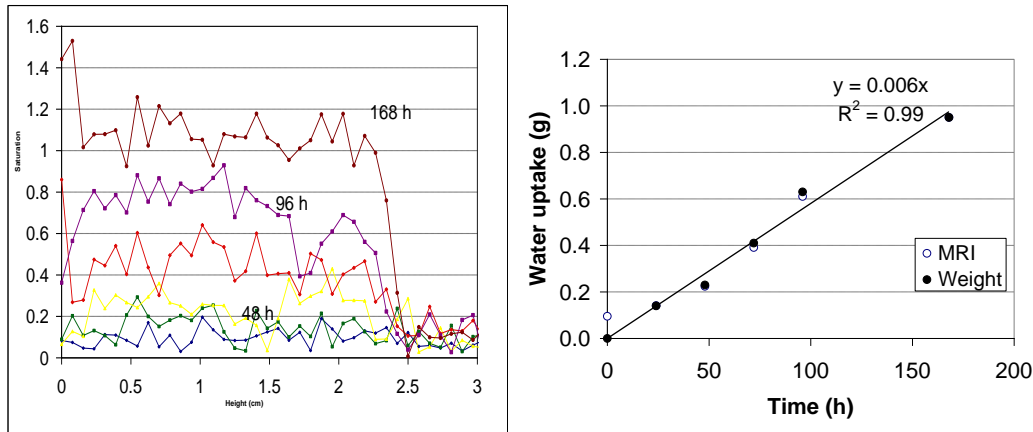

Figure1. left: MRI saturation profiles of the water uptake in contact with water vapor of salt contaminated sandstone (0.256 g NaCl as subflorescence) at T=21°, RH=100% as a function of the height within the sample. right: the rate of water uptake by MRI and weight measurements.

Following the dissolution of the salt crystals by either method, the samples are dried at RH~ 48%, T ~21°. After 3 to 6 subsequent saturation/drying cycles, the percentage of damage is assessed by gently removing salt efflorescence, washing out the remaining salt, drying the stone and weighing the stone. The amount of damage is then given by the weight loss of the stone:

$$\text{Damage} = (M_{initial}^{drystone} - M_{final}^{washedstone}/M_{initial}^{drystone}) \times 100\% \tag{2}$$

The results clearly show that first with humidity cycling the percentage of efflorescence decreases with the progression of the number of cycles from 20% to 5% after 3 cycles. Second, humidity cycling can lead to damage: a 6% loss of materials is observed in the form of sanding. To the contrary, hardly any damage is observed for the case of dissolution with liquid water, followed by recrystallisation (figure 2).

Figure 2. (a) Mšené sandstones after 6 cycles of (a) dissolution/crystallization ; damage < 0.5% of the initial mass (b) deliquescence followed by recrystallization; we observe sanding of the sample (damage~5%).

Figure 3 shows the results of the kinetics of drying obtained both by MRI and weight measurements during drying in cycle 1 (when the sandstone is imbibed with saturated salt solution) and in cycle 3 (after complete saturation of the salt contaminated sandstone in contact with 100% humidity). In most of porous materials, water evaporation takes place at an almost constant rate during a first stage (often down to a very low liquid content); this is the so called constant rate period (CRP) followed by a second stage where the drying rate continuously decreases in time. Here we discuss only the first stage of drying because the special resolution of the MRI measurements of the liquid distribution in the sample does not make it possible to observe how the saturation profiles evolve during the second stage of drying (Shahidzadeh-Bonn et al. 2007, Shahidzadeh-Bonn at al. 2009). In our experiments, although C1 and C3 are done under the same environmental conditions, cycle 1 shows a slower evaporation rate than cycle 3. Two regimes can be observed for cycle 1: at first there is a constant drying rate period CRP1 followed by a much slower drying rate CRP2 (slower by an order of magnitude) as soon as crystallization starts to take place in the pores and at the surface. The CRP is mainly results from the liquid transport through the porous network toward the free surface of the sample. Clearly, in the second CRP2, the crystallization slows down the evaporation, probably just by blocking part of the pores, both within and at the surface of the porous medium. For cycle 3, a much faster drying is observed. The CRP regime continues until the complete desaturation of the sample. The moment that the crystallization starts within the sandstone is not visible in the curve.

The MRI experiments indeed show that for the first cycle the desaturation is not homogeneous; Figure 3 compares the MRI profiles for C1 and C3 at the same saturations; because of the blocking of the pores by the crystallization; the capillary rise that would lead to a homogeneous saturation in the sample is hindered in C1 This slows down the evaporation. As it can bee seen in profiles obtained after 3 cycles, this effect disappear and an almost homogeneous desaturation is observed. The crystallization seems to start later, compare to cycle 1, for saturation around 0.6 at the top of the sample.
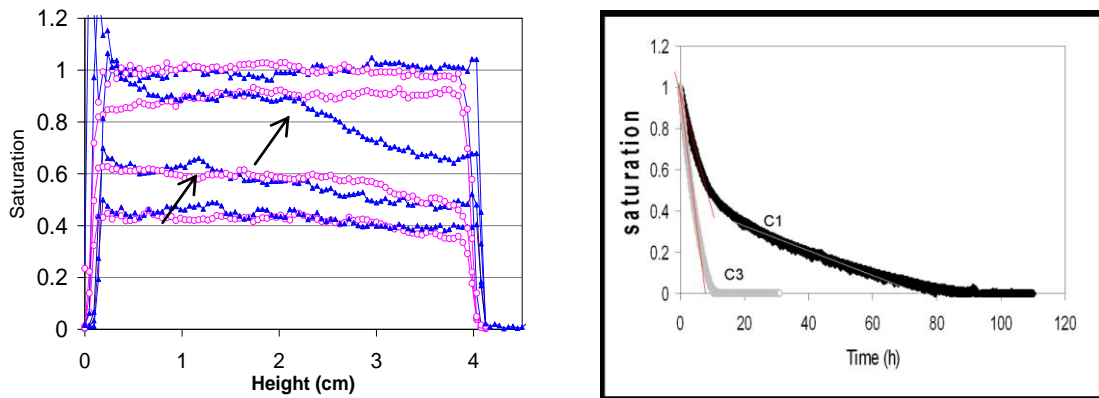

Figure 3. Drying of sandstones: cycle 1 (C1 triangle): imbibed with saturated NaCl solution; Cycle 3: (circle): after complete saturation in contact with water vapor of the salt contaminated stone. On the left the stauration profiles as function of the height; on the right the weight measurements (sample 2x2x4 cm).

3.2. Microscopic experiments

To see what these effects are due to, we now focus on the microscopic features of the rewetting/drying cycles. The dynamics of crystallization were followed at the microscopic scale in capillaries (as explain in experimental section) with the same procedure as for the macroscale experiments: either by rewetting with pure water, or with water vapor.

To mimic a first cycle (C1), a microdroplet (0.1µl) of saturated NaCl solution is deposited on a hydrophilic glass slide under the microscope. The crystallization process starts very rapidly (within few seconds) close to the contact line of the drop and results in the formation of large amount of small cubic microcrystals (of size 30 to 200µm) (Figure 4 C1). The speed of growth of these crystals, as determined from the microscopy images in one crystalline direction is around $0.56\pm0.14\mu ms^{-1}$. At the end of drying, a ring-like crystalline deposit at the border is observed. This is reminiscent of the well-know "coffee-stain effect" (Bonn et al. 2009, Deegan et al. 1997), which is usually attributed to a capillary flow from the center to the border of the drop driven by loss of solvent by evaporation, in combination with pinning of the contact line (the border of the drop). The latter results in a higher concentration of the solute near the edge of the drop and the formation of these crystallites close to the contact line (Shahidzadeh-Bonn et al. 2006, Deegan et al. 1997, Berteloot et al. 2008).

To start the second cycle, a small climatic chamber at 100% relative humidity is put above these crystals under the microscope and the deliquescence of microcrystals is followed in time. The adsorption of water vapor starts rather rapidly, first at the edges and corners of crystal; water is observed to spread over the crystal surfaces to form a continuous film of water which covers every small crystal. These now act as points at which water is going to condense. The rate of dissolution during deliquescence is about 0.27 ± 0.03 μms^{-1}, leading to the formation of a microdroplet of saline solution. After complete deliquescence of the microcrystals, the resulting microdroplet of NaCl solution is consequently evaporated (cycle 2) under the same conditions as in C1 (50±5% HR and 21°C). The microdroplet evaporates and becomes more and more concentrated concomitant with a strong retraction of the contact line. This shows that the contact line is not pinned on defects of the surface. After roughly 120s of evaporation, a rapid growth, $1.25\pm0.04\mu ms^{-1}$, of only two NaCl crystals can be observed (figure 4C2). These nuclei again start to grow near the contact line, as the evaporation is most rapid there. At the end of drying these crystals can reach a size of 350µm, much larger than crystals in C1. These crystals are almost perfectly cubic, suggesting that they are single crystals. It should be noted that these growth rates are measured at beginning of crystallization for each cycle after the crystal has achieved a nominal size that can be observed under the microscope (figure 5).
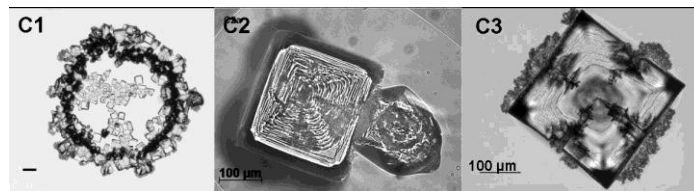

Figure 4. C1: drying of saturated NaCl microdroplet; C2 and C3 : drying after deliquescence of salt crystals. The number of nuclei decreases and the crystal size increases with the progression of cycles.

If we perform a third cycle (C3) of deliquescence and drying on these two crystals, we obtain only one high-quality single crystal (Figure 4 C3). During the deliquescence, the rate of dissolution of the crystals remains the same (on the order of a fraction of a μms^{-1}) but because of the larger size of crystals the complete deliquescence takes a somewhat longer time. During the third drying step a longer time is needed before the nucleation starts (200-300 s); again the droplet retracts, probably leaving some of the impurities on the surface. Only when high

supersaturations are reached we observe the relatively fast growth $2.09\pm0.04\mu ms^{-1}$ of a single NaCl crystal. The size of the crystal at the end of drying can be as large as $\cong500\mu m$.

The rapid growth in the cycle 3 happens because the growth rate is proportional to the supersaturation (; Al-Jibbouri & Ulrich 2002). These results show clearly and for the first time that during deliquescence/crystallization cycles the number of crystals decreases, whereas the growth velocity increases with the number of the cycles. Since, the evaporation time before the crystallization in C2 and C3 is longer, a higher supersaturation can be reached before the formation of a critical nucleus and subsequent growth (Figure 4). Because of the formation of a smaller number of nuclei, the crystals are observed to grow to larger sizes in order to consume the supersaturation during evaporation .The impurities which are expelled from the single crystal condense at the end of the crystallization forming a white film composed of large amount of very small microcrystallites, similar to efflorescence (Figure 4C3).
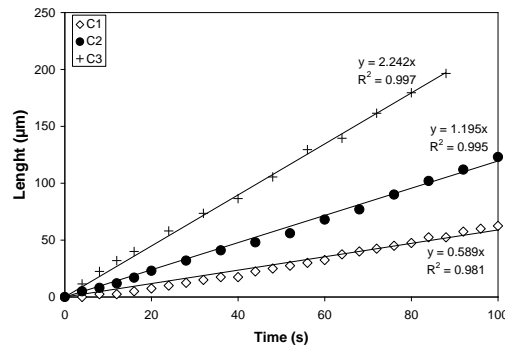

Figure 5: Dynamics of crystallization growth in a microdroplet for three cycles of deliquescence/recrystallization. The growth rate of crystals, increases with the progression of cycles

Experimentally, it was shown that the growth rate of crystals increases linearly with increasing supersaturation of the solution, (Al-Jibouri & Ulrich 2002, Deasarnaud & Bonn 2011). In our experiments, we have calculated the salt concentration in droplets at the moment that the crystal starts to grow, by knowing: (a) the evaporation rate, ($3.5\ 10^{-4}\ \mu l.s^{-}$ from the measured drop radius, assuming that the contact angle remains constant during evaporation (Shahidzadeh-Bonn et al. 2006)) (b) the initial droplet volume at saturation S=1 and (c) the evaporation time before nucleation. The calculation gives a supersaturation ($S=C_t/C_{sat}$) of $S\sim1.6\pm0.2$ in cycle 2 when 2 or 3 crystals start to grow in the solution and $S\sim2.6\pm0.2$ in cycle 3 when a single crystal grows in the droplet.

In the series of experiments on which dissolution is achieved by adding pure water on crystals, one would expect that if a water droplet is added onto the existing crystals, part of the contact line may find defects on the substrate again; these now compete with the crystallites that also pin the contact line. Therefore, one anticipates that the mechanism of forming single crystals by repeated cycling may still work, but should be less efficient. This is indeed what we have observed experimentally when rewetting is done with liquid water. Although less crystals (2, 3 or 4) are obtained with cycling, the formation of single crystal is hardly reached after 4 or 5 cycles. Consequently, hardly supersaturations higher than 1.6 ± 2 is reached.

We have also performed the same series of experiments in a confined geometry: These experiments have been done in square microcapillaries ($100\mu m$) as simple model systems for a single pore within a porous medium. Same results and conclusion than for microdroplets are obtained which confirm clearly findings reported here (figure 6).
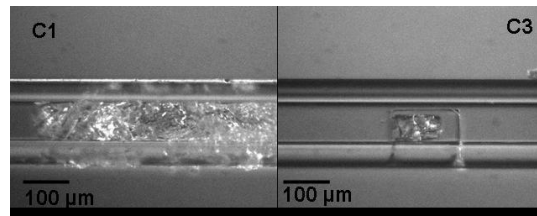
Figure 6: Humidity cycling in square microcapillary. C1=cycle 1; C3=cycle 3.

4   CONCLUSIONS

In this paper we have shown that the key of understanding of why the same salt can cause damage in some conditions and not in others is the kinetics of crystallization which plays an important role in the degradation. This opens the way to a better understanding of salt damage by the two important salts NaCl and Na_2SO_4, but also suggests how to best desalinate contaminated stones depending on the nature of the salt.

In our previous work (Shahidzadeh-Bonn et al 2010), we have demonstrated that sodium sulfate with hydrated and anhydrous phases can lead to severe damage in porous materials during rewetting /drying cycles because of the only partial dissolution of anhydrous crystals in regions (pores) that are highly concentrated in salt. The thenardite microcrystals dissolve very rapidly, and in part act as seeds to form large amount of hydrated crystals creating grape-like structures that expand rapidly. These clusters generate stresses larger than tensile strength of the stone, which leads to the damage. On the other hand, with humidity cycling after slow deliquescence followed by recrystallization the experiments reveal the direct formation of isolated anhydrous crystals (thenardite). The crystallization of the anhydrous salt generates only very small stresses that hardly damage the stone (Desarnaud et al, 2011).

On the contrary, for sodium chloride, here we have shown that damage on Prague Sandstone is found to occur rather during humidity cycling than rewetting/ drying cycles. Detailed observations in fact show that using liquid water for rewetting less or no damage is observed whatsoever, in line with our findings reported here. These results show for the first time that subsequent humidity cycling leads to the growth of salt crystals by expulsing impurities. The consequence of that is the faster growth of less nuclei with the progression of cycles leading to larger crystals and higher supersaturations before nucleation and growth. As a consequence, the crystallization pressure increases with increasing the number of cycles; one then reaches crystallization pressures in excess of the tensile strength of the Prague sandstone. This process allows us to obtain only one single crystal instead of several dozens of crystallites in as little as three cycles. The impurities which are expelled from the single crystal condense at the end of the crystallization forming a white film composed of large amount of very small microcrystallites, similar to efflorescence. It can be concluded that deliquescence/recrystallization clearly favors salt crystals purification (Desarnaud and Shahidzadeh-Bonn 2011). The results reported here give also a clue why, in the presence of NaCl, subsequent humidity cycling leads to an irreversible dilation and the gradual expansion of the material (Lubelli et al 2006).

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