STUDY OF KINETICS OF SALT CRYSTALLIZATION DURING REWETTING DRYING AND HUMIDITY CYCLING

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Abstract

In this paper, we reveal the major role the recrystallization dynamics plays in the way different salts cause damage to stone under different environmental conditions. There are two ways in which a salt, once crystallized, can take up water again: by bringing it in contact with liquid water (dissolution) or with water vapour (deliquescence). We compare the kinetics of salt recrystallization for different salts (NaCl. KCl, Na2SO4), after either deliquescence or dissolution followed by drying, for several cycles.

We find that deliquescence/recrystallization with humidity cycling leads to the growth of salt crystals by expulsing impurities; after only a few cycles we obtain high-quality single crystals for salts such as NaCl and KCl that have only a one crystalline form. In this process, the solution reaches high supersaturations before the crystal growth which in turn leads to a higher crystallization pressure and hence damages the stone. These results show why subsequent humidity cycling with NaCl leads to an irreversible dilation and the gradual expansion of the material.

For Na2SO4 which has different crystalline forms, the fact that high salt concentrations are reached during deliquescence followed by drying, favors the direct precipitation of anhydrous Na2SO4. The crystallization of the anhydrous salt generates only very small stresses that hardly damage the stone. However, for sodium sulfate rewetting/drying leads to severe damage because the thenardite microcrystals dissolve very rapidly, and remaining crystals 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.

These results shed some light on how the kinetic pathway of crystallization plays an important role on the way the same salt can cause in some conditions and not in others

Keywords: sandstone, dissolution, deliquescence, recrystallization kinetics of crystallization, salt weathering

1. Introduction

Salt crystallization in porous construction materials is the principal process of masonry, mortar, cements degradation (Goudies and Viles 1997; Novak and Colville 1989). In civil engineering salt weathering has been recognized as one of the major cause of highways and bridges decay. Salts can be be naturally present in the materials used for construction (such as mortars and bricks) or can derive from external sources (capillary rising ground water, eolian origin, sea water along rocky coasts, and atmospheric and soil pollution). It is well know that repeated cycles of wetting/dying of salts that are present in the stones can provoke severe damage of building materials

(Shahidzadeh-Bonn et al. 2010; Espinosa Marzal and Scherer 2008; Steiger 2005; Scherer 2004; Lubelli et al. 2004; Flatt 2002). There are two ways in which salt, 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. Consequently, when environmental conditions such as humidity or exposure to rain or rising damp vary, salts can dissolve and cause damage to the material by re-crystallization upon drying. In practice, when the crystallization takes place within the porous medium, a phenomenon called subflorescence, the weathering is usually believed to be more harmful than when salts crystallize on the exterior of the porous network (on the walls of the stones), a phenomenon known as efflorescence.
The involved mechanism is under investigation since decades and still unclear.

The most accepted theory is the crystallization pressure of the crystal against the pore wall, which is proportional to the degree of supersaturation of the salt solution (Scherer 2004; Rodriguez Navarro et al. 2000; Hamilton et al. 2010; Lubelli et al. 2006; Steiger 2005b; Camassel et al. 2005).

In fact, 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:

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

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 ($S = C/C_{sat}$).

For a given supersaturation, by taking into account the non-ideal behaviour of the liquid phase, the total number of ions present and the interactions, the crystallization pressure due to the crystal growth may be expressed as (Steiger 2005):

$$\Delta P = \frac{\nu RT}{V_m} (\ln\frac{C}{C_0} + \ln\frac{\gamma_\pm}{\gamma_{\pm,0}} + \frac{\nu_0}{\nu}\ln\frac{a_w}{a_{w0}}) \qquad (2)$$

Where n is the total number of ions per dissolved molecule (2 for NaCl and 3 for Na_2SO_4) and V_m the molar volume of the crystalline phase. The first term in the parenthesis describes the supersaturation in terms of concentration, the second and third terms describe the non ideal behaviour of the concentrated salt solutions.

Although the existence of a supersaturation can account for an excess pressure exerted by the salt crystals against the pore walls (Steiger 2005b; Rodriguez Navarro et al. 1999; Coussy 2006; Camassel et al. 2005) and hence the damage, this mechanism can not explain :

1- Why, same salt can cause damage in some conditions and not in others (Shahidzadeh-Bonn et al. 2010, Steiger 2005; Flatt 2002; Lubelli et al. 2006; Desarnaud et al. 2011a.)
2- Why, some salt (as Na2SO4), in same environmental conditions, are more damaging than other (as NaCl which should develop a higher crystallization pressure) (Steiger and Asmussen 2008).

Besides the difference in the degree of damage, some authors have in addition reported more efflorescence in the case of sodium chloride whereas others mention more efflorescence in the case of sodium sulfate contaminated stones (Shahidzadeh-Bonn et al. 2008; Shahidzadeh-Bonn et al. 2010; Scherer 2004; Lubelli et al. 2006; Rodriguez Navarro et al. 1999; Camassel et al. 2005).

Consequently, a detailed understanding of how crystal growth within the porous media leads to damage still remains elusive.

The objective of this study is to elucidate the role played by the kinetics of salt crystallization in the damaging process. For this purpose, we have followed the kinetics of sodium sulfate and sodium chloride crystallization during dissolution/ drying and deliquescence/drying cycles and we have related the results to those obtained at macroscopic scale on sandstone.

2. Experiments

We present here a multiscale study on sodium chloride and sodium sulfate of which we investigate the effect of recrystallization on both macroscopic and microscopic scales.

- In the case of humidity cycling, the samples were put in contact with liquid water in climatic chamber at T=21°C and RH~ 100%. For RH above the equilibrium relative humidity of both salts ($RH_{eq\ NaCl,\ sat}$~ 75%, $RH_{eq\ Na2SO4,\ sat}$~ 95% (Mullin, 1992)) salts deliquesce and the samples take consequently water. The saturated samples are again dried at RH~48%. The humidity cycling was repeated 6 times.

- In the case of dissolution/recrystallization cycling, the samples were subsequently rewetted by imbibition with pure liquid water until complete saturation. Then the samples is dried at T=21°C and at RH~48%. The dissolution/recrystallization cycles was repeated 2 times.

The macroscale experiments consist of studying the behaviour of salt contaminated sandstones. The salt contaminated samples were prepared by impregnation with saturated salt solution (NaCl: 6.1 M; Na_2SO_4: 1.4 M) followed by drying at T=21°C and Relative Humidity RH~50 ± 2 % in a homemade climatic chamber in which both temperature and humidity are imposed (Shahidzadeh and Desarnaud 2012). The global drying kinetics were followed in each cycle on an automated balance with a precision of (±0.001 g) that is places inside of the humidity chamber and that is read out automatically by a computer.

In addition, Proton MRI (Magnetic Resonance Imaging) was used to follow the saturation profiles during water uptake and subsequent drying cycles (Bonn et al. 2008). For sodium sulfate with different hydrated and anhydrous phases, the comparison of the evaporation rates calculated from the MRI and weight measurements can give relevant information about the formation of hydrated crystals in the porous network, as the protons in the hydrated crystals do not significantly contribute to the proton MRI signal, but of course do contribute to the weight. As we have shown previously the water present in the hydrated crystals does not contribute to the measured proton density, because their NMR relaxation time becomes very short; they do of course contribute to the measured weight (Shahidzadeh-Bonn et al. 2010).

The microscale experiments consist of using phase contrast microscopy and direct imaging to study the kinetics of deliquescence (humidity cycles) and dissolution

(dissolution /recrystallization cycles) of salts crystals (NaCl and Na_2So_4) entrapped in a square microcapillaries (100μm) followed by recrystallization during the evaporation. Hydrophilic microcapillaries were used as a simple model system for a single pore in a porous medium. One of the key features of pores in porous media is the existence of axial channels or grooves that can retain wetting liquids. In square microcapillaries, due to capillary forces, the wetting phase has a tendency to collect in the edges by forming a thick film when a non-wetting phase such as air invades a fluid-saturated capillary tube.

3. Results
3.1 Macroscale experiments

During a first cycle (C1), the sandstone samples were saturated by imbibition with saturated salt solutions (prepared in the laboratory (6.1 M for NaCl) or (1.4 M for Na_2SO_4)) and left to dry. The amount of efflorescence for sodium chloride (~ 20% ± 2% of the initial mass of salt) remains less important than for sodium sulfate (~ 50% ± 5%). This was explained because of the decrease of the surface tension of the liquid once crystallization starts in the solution. The decrease of the surface tension of the liquid leads to the increase of the spreading power of the solution which can favour the efflorescence. It was shown experimentally that this effect is much pronounced for sodium sulfate than sodium chloride which consequently leads to more efflorescence (Shahidzadeh-Bonn et al. 2008). This efflorescence is gently removed with a toothbrush. Salt contaminated stones 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 with pure water 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 around 60-80 days for these samples (2x 2 x 4 cm) and is found to depend on the quantity of salt present as subflorescence (Desarnaud and Shahidzadeh -Bonn, 2012).

Following the dissolution of the salt crystals by either methods, 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:

$$\text{Damage} = (\, M_{initial}^{drystone} - M_{final}^{washedstq} / M_{initial}^{drystone}\,) \times 100\%$$

3.1.1 Humidity Cycling

For stones contaminated with Na_2SO_4, our experiments reveal hardly any damage (<0.5%) (Figure 1) whereas humidity cycling can lead to 6% loss of materials for NaCl in the form of sanding. For the case of sodium chloride, these results are in good agreement with previous results obtained by Lubelli et al. 2006 who have shown that in the presence of sodium chloride subsequent humidity cycling leads to an irreversible dilation and the gradual expansion of the material provoking the granular disintegration of the stone. The local water saturation during water uptake and drying cycles in the stone samples was followed using Proton MRI for each cycle (Shahidzadeh-Bonn et al. 2010). For both salts, the evaporation rates calculated from saturation profiles agree nicely with those obtained from weight measurement. In the following cycles, with

humidity cycling experiments, no discrepancy is observed between the two methods. It suggests that with humidity cycling, only anhydrous crystals of sodium sulfate (thenardite) start to grow within the porous network after total deliquescence of crystals.
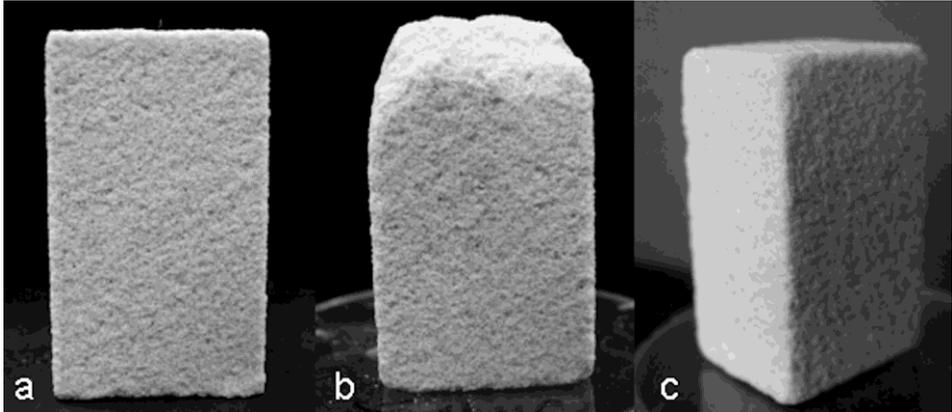
Figure 1. (a) Prague Sandstone sample (2x2x4 cm^3) before the experiments. After (b) 2 dissolution/Recrystallization cycles and (c) 2 humidity cycles imbibing with Na$_2$SO4. (b)Severe damage (loss of material), (c) hardly any damage

3.1.2   Dissolution/Recrystallization cycling

The results are the opposite of what we have obtained with humidity experiments. Indeed, for stones contaminated with Na$_2$SO$_4$, after 2 dissolution/crystallization cycles our experiments reveal a significant disintegration of the stone (Figure1). The damage can be up to 10-12%. For the stones contaminated with sodium chloride, although a larger amount of salt was present as subflorescence, no measurable damage occurred after 6 dissolution/crystallization cycles.

For Na$_2$SO$_4$ contamined sandstones, in C1, there is a serious discrepancy between the rate of evaporation from the MRI profiles and weight measurements. The difference between MRI and weight measurements can be in fact attributed to the formation of hydrated crystals that are not visible with the MRI.

3.2 Microscale experiments

We now focus on the microscopic features of the rewetting/drying cycles. The dynamics of crystallization of NaCl and Na$_2$SO$_4$ 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.

Salts were entrapped in the microcapillary during a first cycle of evaporation of a known volume of saturated solution. In contact with water vapor or liquid water, salt crystals dissolve which leads again to the formation of salt solution in the microcapillary.

3.2.1   Humidity cycling

When crystals are rewetted with vapour water, sodium sulfate and sodium chloride solutions show similar behaviour: after complete deliquescence the saturated salt

solutions evaporate for a long period of time without any nucleation and growth of crystals. This implies that the salt concentration in the solution increases; one of the consequences of this is an increase in the liquid-vapor surface tension γ_{lv} of the solution (Shahidzadeh-Bonn et al., 2008). This in turn leads to an increase in the contact angle of the liquid on the glass walls, as given by Young's equation (Sghaier et al., 2006). During the evaporation, if the contact line is not anchored on defects on the surface (which is the case in these experiments), the contact line of the wetting films in the corners then retracts in the capillary. These results occurred with those obtained in the same conditions in droplets (Desarnaud et al. 2011b).

For sodium chloride, subsequent cycles of recrystallization lead to smaller number of nuclei which grow to larger sizes in the microcapillary (Figure 2).
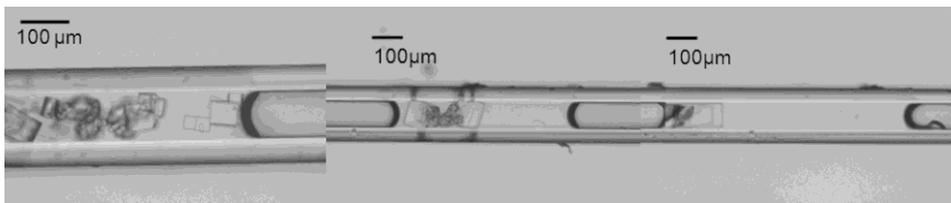
Figure 1. Humidity cycling in a square microcapillary: (a) C1, first cycling of drying, formation of a large number of small cubic crystals, (b) C2, second drying cycle, growth of two larger crystals, (c) C3, last drying cycles, growth of only one big cubic crystal.

We observe that the speed of growth at the start of the crystallization is two orders of magnitude larger in the last cycle ($\sim 5.0 \pm 0.5$ μms^{-1}) than at the first cycle ($\sim 0.044 \pm 0.003$ μms^{-1}) which correspond to a local supersaturation of 6.2 mol.l^{-1} and 0.062 mol.l^{-1} respectively (Al-Jibbouri and Ulrich, 2002). Based on Steiger, 2005 the crystallization pressures in contact with a NaCl-solution at S~2 (Cycle 2,3,4) and S~1.01 (cycle1) are respectively $\Delta P= 228$ MPa $\Delta P= 1.8$ MPa. From this calculation we can only conclude that in fact with cycling and because of the very large supersaturations, very large crystallization pressures can be reached. However, one should realise that this value corresponds to the starting point of crystallization and the stress will obviously decrease with consumption of the supersaturation by the crystal growth (Shahidzadeh and Desarnaud, 2012). Apparently impurities are expelled in each cycle (as in classical recrystallization for the purification of salts); we therefore observe the formation of a smaller number of nuclei and the crystals are observed to grow to larger sizes as the number of cycle increases.

For sodium sulfate, our microscale experiments reveal that in C1, hydrated crystals are formed which is evident from their crystal shape (Rodriguez Navarro, et al., 1999, Shahidzadeh-Bonn et al., 2008) The growth rate of these crystal is about ~0.024 μms^{-1} which corresponds to a supersaturation of 0.019 mol.l^{-1} (Rosenblatt et al., 1984) and a crystallization pressure of $\Delta P=0.12$ MPa (Steiger, 2005) which is not sufficient to decay the sandstone (tensile strength of our sandstone = 0.9MPa (Shahidzadeh-Bonn et al., 2010)). Afterwards, these hydrated crystals lose their water and transform onto anhydrous crystals after complete evaporation.

With humidity cycling after a slow and total deliquescence of crystals, even though the solution can achieve a very high concentration before recrystallization (a

supersaturation of S~3 with respect to the formation of the hydrated phase) hydrated crystals do not precipitate. As it is obvious from the shape of the crystals shown recrystallization leads to the growth of the anhydrous phase (dendritic-shape, or phase III) (Desarnaud and Shahidzadeh-Bonn, 2012b) which is subsequently transformed into the stable rhombohedral-shape (phase V). According to the phase diagram of the different crystalline phases of sodium sulfate, the high salt concentration of ~4.2M that we reach in the solution before nucleation allows for the precipitation of the anhydrous phase: the solubility of thenardite Phase V is ~3.7 M (Steiger 2005).

   The reason why the precipitation of hydrated crystals is hindered with such a high supersaturation is not known, and is under investigation. Clearly, even though the formation of mirabilite should be favored thermodynamically, kinetically the formation of thernardite appears to be favored from such concentrated solutions. In addition, the direct formation of anhydrous crystals at pore scale agrees very well with our MRI and weight measurement in sandstones at the macroscopic scale. The growth rate of the rhombohedral shape was measured in two directions, at the beginning of growth; a mean value of ~0.9±0.1 μms^{-1} is found which corresponds to a supersaturation of S~1.065 (Rosenblatt et al., 1984) and a crystallization pressure of ΔP=8.8 MPa from (Steiger 2005). However, 8.8 MPa is still in excess of the tensile strength of our sandstone (0.9MPa (Shahidzadeh-Bonn et al. 2010)), so we do not know why no damage is observed even after several cycles.

3.2.2 Dissolution/Recrystallization cycling

   The rewetting with liquid pure water of capillary containing crystals is a very fast phenomenon. When the existing NaCl crystals are put in contact with liquid pure water, less crystals (2, 3 or 4) are obtained with cycling, the formation of single crystal is hardly reached after 4 or 5 cycles. Consequently, the supersaturations reached are not high. Part of the contact line may find defects on the capillary walls again; these now compete with the crystallites that also pin the contact line. The mechanism of forming single crystals by repeated cycling still works, but is less efficient.

For Na$_2$SO$_4$, there is a partial and rapid dissolution of the anhydrous microcrystallites in the regions that are highly concentrated in salt. The remaining thenardite small crystallites acts as seeds to form large amount of hydrated crystals creating grape-like structures that expand rapidly (Figure 3).
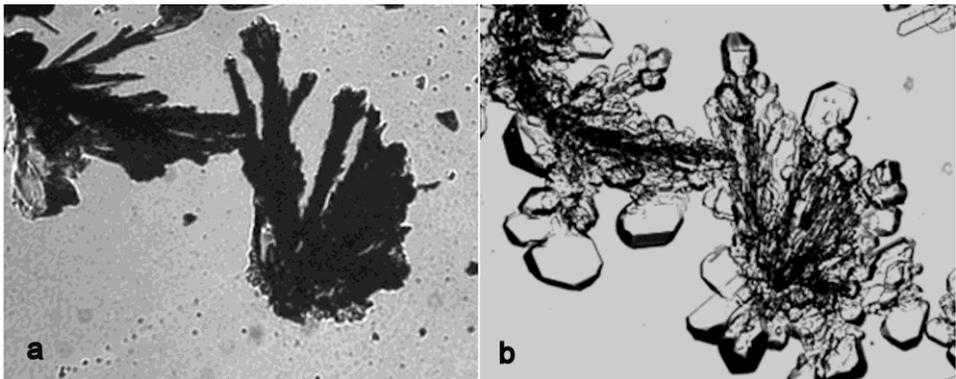
Figure 3. Microphotographs of anhydrous NA_2SO_4 crystallites formed after dehydration of the hydrated crystals in C1.(b) C2, After rewetting with pure water, growth of large hydrated crystals from the non-dissolved anhydrous crystallites, which forms a big cluster

The growth rate of hydrated crystal in the grape structure is found to be at least one order of magnitude larger than in the first cycles: $0.26\mu ms^{-1}$ (Shahidzadeh-Bonn et al. 2010). The corresponding supersaturation is $0.21mol.l^{-1}$ (Rosenblatt et al. 1984), resulting to a crystallization pressure of $\Delta P \sim 1.40$ MPa (Steiger 2005), sufficient to damage the sandstone, as indeed observed experimentally.

4. Discussion and Conclusions

In this paper we show the importance of the kinetics of salts crystallization in the understanding of stone damage.

The deliquescence being a very slow process it leads to the formation of an homogeneous salt solution. It allows to obtain very high concentration of the solutions before recrystallization upon drying. For sodium chloride with one crystalline phase, this leads to a faster growth of a smaller number of larger nuclei when the number of cycles increases. The growth of such very large crystals could explain the damage observed in the sandstone.

On the other hand, when crystals are rewetted with liquid pure water, the dissolution is very fast process resulting in a more heterogeneous solution compared to deliquescence. We show that the dissolution of sodium chloride with pure liquid water does not lead systematically to less nuclei with larger crystals (Desarnaud and Shahidzadeh-Bonn, 2011b) that could explain why no damage occur on sandstone in this case.

For the sodium sulfate, with both hydrated and anhydrous phases, the results show that hardly any damage occurs for deliquescence/crystallization cycles whereas dissolution/crystallisation cycles can lead loss of material due to granular disintegration.

In the humidity cycling experiments (slow process), after slow deliquescence, the homogeneous solution reaches high salt concentrations before recrystallization, the crystalline phase with the higher solubility (thenardite) is formed; however the crystals remain relatively small. These small crystals are observed not to lead to significant damage of the sandstone.

When the rewetting is done with liquid pure water (fast process), there is a partial dissolution of the entrapped anhydrous crystals which can locally create regions that are supersaturated with respect to the hydrated phase. Consequently, in the heterogeneous salt solution which is subsequently formed, the remaining crystals are observed to act as nucleation points to form a large amount of hydrated crystals creating grape-like structures that expand very rapidly. The clusters of hydrated crystals have a much bigger volume than thenardite which can explain the observed damage in these rewetting/drying experiments.

These experiments reveal that it is both the crystals size and the kinetics of salt crystallization than the direct crystallization pressure that is important and could explain the degradation.

These results shed some light on how the kinetics pathway of crystallization of $NaCl$ and Na_2SO_4 influences the way these salts cause damage under different environmental conditions

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