

SALT WEATHERING OF SANDSTONE DURING DRYING: EFFECT OF PRIMARY AND SECONDARY CRYSTALLISATION

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Abstract

In this study we show that the key to understanding why the same salt can cause damage in some conditions and not in others is the kinetics of recrystallisation. Salt-contaminated porous materials are known to deteriorate with environmental fluctuations. Salts can be naturally present in the materials used for construction or can be derived from external sources. With changes in climate, entrapped salt crystals can once again form a salt solution after contact with liquid water (dissolution) or with water vapour (deliquescence). The solution is mobilized in the porous network and then salts re-crystallize with drying. We present both macroscopic and microscopic experiments assessing the recrystallisation dynamics of NaCl in sandstone with wetting-drying and humidity cycling. Advanced techniques such as high resolution X-ray computed tomography and Scanning Electron Microscopy are used to study the recrystallisation process in the porous network in parallel with the drying kinetics. Our results show that recrystallisations following deliquescence and dissolution lead to very different crystallisation patterns. With humidity cycling, recrystallisation promotes the formation of localised bigger cubic crystals in the subsurface of the stone, whereas rewetting leads to efflorescence in the form of large localised ‘cauliflowers’ at the surface. The different growth dynamics have direct consequence on the drying behaviour of the sandstone and its deterioration.

Keywords: Mšené sandstone, salt weathering, drying and deliquescence kinetics, crystallisation pattern

1. Introduction

Salt crystallisation inside confined systems is one of the major causes of mechanical or physical weathering causing disintegration of porous rocks and building materials (Goudies and Viles, 1997; Shahidzadeh-Bonn *et al.*, 2010) It is also the most important forms of soil

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degradation (Cook and Smalley, 1968) and problems for oil well productivity and CO₂ sequestration (Peysson, 2012).

With the variation of climatic conditions such as relative humidity, or rain followed by drying, the salts present in porous media crystallize either in the form of efflorescence (at the surface) or subflorescence (within the pore network) (Rodriguez-Navarro and Doehne, 1999). Once crystallized, salts can re-dissolve in two different ways: by contact with liquid water (dissolution) or by contact with water vapour (deliquescence). The latter is due to the hygroscopic properties of salts. The resulting salt solution is then mobilized in the porous network and salt subsequently re-crystallizes on drying.

The action of salts on weathering of porous media has attracted a lot of attention over the past decade, but remains incompletely understood. Most studies reported in the literature deal either with unidirectional (1D) evaporation of a porous material that is permanently supplied with the salt solution or with evaporation-wicking experiments (Eloukabi, *et al.*, 2013; Shokri, 2014).

These studies have revealed the impact of the pore size and the relative humidity on the type of crystallisation. Mainly efflorescence has been observed in different types: crusty or patchy (Verran-Tissoires and Prat, 2014) (also referred to as ‘cauliflowers’) (Shahidzadeh-Bonn *et al.*, 2008) and although it has been observed that the crystallisation affects the drying rate, there are still many aspects that need to be clarified in order to understand the interplay between salt crystallisation and evaporation. The dynamics of the crystallisation and recrystallisation processes (Mullin, 2001) have not been studied yet. In general, recrystallisation that results from cycling differs from the initial crystallisation (Desarnaud and Shahidzadeh-Bonn, 2010). Moreover if the nucleation is primary (directly from solution) high supersaturations can be achieved (Mullin, 2001; De Yoreo and Vekilov, 2003) which is the case for the evaporation of homogeneous salt solutions in confined systems (J. Desarnaud *et al.*, 2014). On the other hand, the secondary nucleation (from pre-existing crystallites present in the solution) typically happens around the saturation concentration (De Yoreo and Vekilov, 2003). It is clear from the above that the crystallisation dynamics in a porous medium depends on both thermodynamic and transport processes. These will have also a direct impact on the evaporation rate of the solvent (water) from the porous network.

In this paper we show that the dynamics of crystal growth is of paramount importance on both the evaporation rate and the possible damage generated by the salt crystallisation. When the same amount of water is used to dissolve the salt present in a stone, different recrystallisation patterns and evaporation kinetics can be found if this is done in different ways: by a rapid saturation with liquid water, or by a slow saturation using water vapour.

2. Experimental Section

We perform a multiscale study on the behaviour of sodium chloride contaminated sandstones. Solutions were prepared with Sigma Aldrich grade 99.9% NaCl and Ultrapure Millipore water. Macroscale experiments consist of studying the crystallisation pattern and the drying kinetics of saturated sandstones (porosity $\phi \sim 29\%$, and pore diameter $d_p \sim 30 \mu\text{m}$). We study the recrystallisation behaviour and the drying of the salt-contaminated sandstones once they were rewetted with liquid water or brought in contact with water vapour ($RH \sim 100\%$). The global drying kinetics (evaporation in 3D directions)

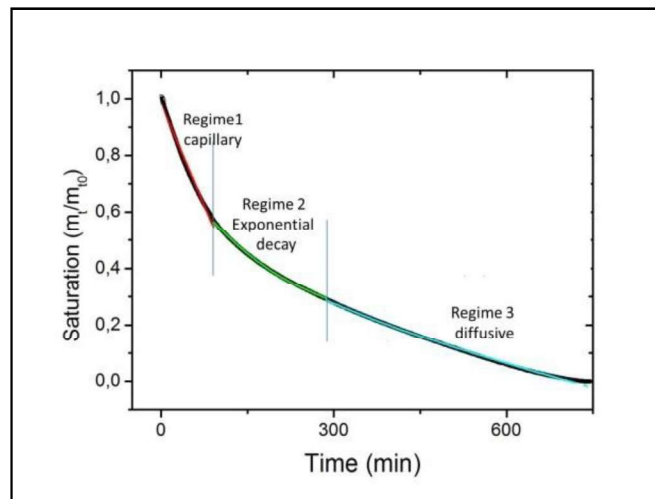
are followed on an automated balance with a precision of 0.001 g placed in a homemade, controlled climatic chamber at $T=21^{\circ}\text{C}$, at $RH\sim 20\%$ (Shahidzadeh and Desarnaud, 2012). We have investigated the crystallisation in the core of the stone and at the surface in more detail using high resolution X-ray computed tomography ($\mu\text{-CT}$), optical and Scanning Electron Microscopy (SEM) combined with EDS. X-ray $\mu\text{-CT}$ was performed at the Centre for X-ray Tomography at the Ghent University (UGCT) using the scanner HECTOR (Desarnaud *et al.*, 2015). We also performed microscale experiment using square microcapillaries (100 μm) as simple model systems for a single pore within a porous medium, to investigate the kinetics of dissolution and deliquescence of crystals, followed by recrystallisation. Quantifying small-scale features is fundamental to improving our understanding of the underlying basis of macroscopic fluid and solute transport behaviour.

3. Results

3.1. Macroscale experiments

3.1.1. Crystallisation

During a first series of experiments, the sandstones samples are saturated by imbibition with NaCl solutions (at saturation: 6.1M). At $RH\sim 20\%$ the drying behaviour of the sample consists of three regimes: first a continuous constant drying rate period (CRP) until the residual saturation is roughly half of the initial saturation. In the second regime the saturation no longer decreases linearly in time, but follows an exponential decrease. The third regime is much slower: a $t^{1/2}$ dependence of the saturation as a function of time is found, characteristic of a mass transfer limited by diffusion that controls the evaporation (Prat, 2007) (Fig. 1).



*Fig. 1: Evaporation rates at $RH\sim 20\%$. Three regimes are observed
 Regime 1(CRP): $mt/mt_0 = -0,0049t + 0,986$; Regime 2: $mt/mt_0 = 0,79e^{-0,003t}$;
 Regime 3: $mt/mt_0 = -0,026 t^{1/2} + 0,79$.*

This leaves the question what the origin is of the second (exponential decay) regime followed by a diffusive regime for drying at low relative humidity. Microscale analysis of the sample reveals the formation of salt crystals at the surface of the sample (Figures 2a and 2b) and no crystals in the core of the sample (Fig. 2c). The lateral rapid growth of salt crystals forms a skin on the outer surface of the sandstone that makes a barrier and prevents

the fluid from reaching the surface to evaporate (Figures 2d and 2e). In fact, the skin formation accounts for the exponential decrease of the drying rate with time: with the growth of the skin layer the evaporative surface rapidly becomes smaller, which slows down the evaporation. In fact, the drying rate is proportional to the surface of evaporation:

$$\frac{dm}{dt} = -cA \quad (\text{Eq. 1})$$

As soon as crystals start to grow at the surface, the evaporative surface decreases according to:

$$\frac{dA}{dt} = \alpha \frac{dm}{dt} \quad (\text{Eq. 2})$$

Consequently, the combination of these two differential equations for the evaporated mass gives:

$$\frac{d^2m}{dt^2} = -c\alpha \frac{dm}{dt} \quad (\text{Eq. 3})$$

which has an exponential solution: $m = m_0 e^{-c\alpha t}$, as is observed in the experiments.

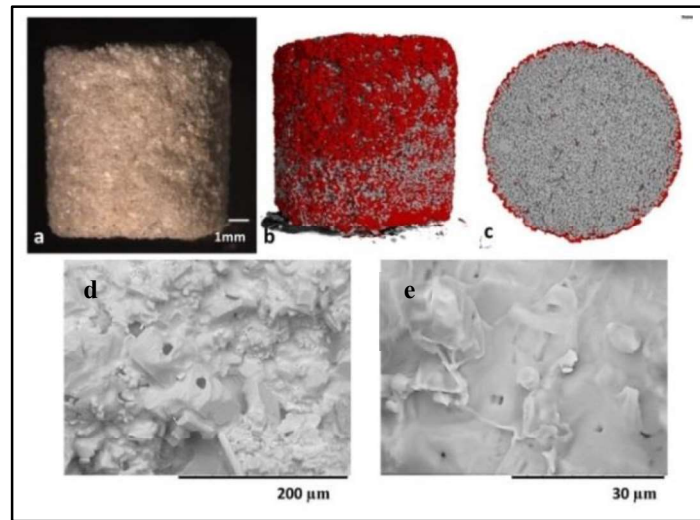


Fig. 2: Samples at RH 20%: a) Sample after drying; b and c) X-ray μ -CT analysis of NaCl at the surface and in the core (middle) of the samples. Below, SEM picture of the porous salt skin after evaporation of saturated salt solution in sandstone.

A more detailed investigation shows that the salt skin which covers the outer surface of the sandstone is in fact also porous with a mean pore size of about $3\mu\text{m}$, i.e 10 times smaller than the pore radius of sandstone (Fig. 2d and 2e). The average thickness of the salt skin was estimated from micro-CT results and SEM images. Both methods give a maximum thickness of the salt skin around $250\mu\text{m} \pm 50\mu\text{m}$. According to Washburn's law (1921) reducing the pore diameter will reduce the speed of fluid transport through capillary suction. Here, the speed of the capillary flow through these small pores is found to be insufficient to overcome the evaporation rate at $RH \sim 20\%$. This leads to rupture of the

wetting films at the outer surface; subsequently diffusive transport of vapour through the small pores controls the drying kinetics in the third regime.

3.1.2. Recrystallisation dynamics

After the initial drying described above, we bring the NaCl-contaminated sandstones in contact either with liquid water (dissolution) or with water vapour ($RH > RH_{eqNaCl}$, deliquescence) until complete saturation. Once saturated, the sample is dried again at $RH = 20\%$. We have repeated this cycling up to 3 times.

Dissolution-drying experiments In the case of saturation by rewetting with pure water which is a rapid process, we observe that independent of the relative humidity, not all salt crystals at the surface will have time to dissolve and distribute through the stone before the evaporation starts. Drying induces the secondary nucleation of new crystals on top of the existing, incompletely dissolved ones. In this situation, low supersaturations and small induction times are observed because the nucleation and growth take place on existing crystal surfaces. The rewetting is done with pure water so no additional salt is added. The observed precipitation of the new crystals at the surface thus implies the dissolution of crystals within the sample and the transport of material to the outer surface where the growth proceeds. Therefore, rewetting followed by drying cycles, tends to extract the salt from within the porous medium towards the outer surface by forming large cauliflower-like salt crystals assemblies at the surface (Figures 3a, 3b, 3c and 3d).

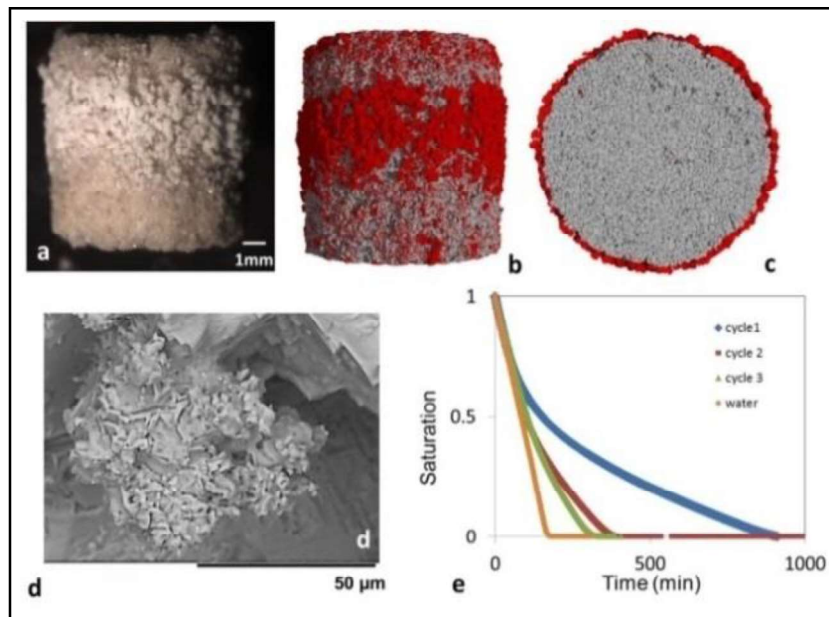


Fig. 3: Recrystallisation due to dissolution-drying cycles at $RH \sim 20\%$; a) crystallisation of cauliflower-like salt crystals; b and c) X-ray μ -CT analysis of NaCl at the surface and in the core of the samples; d) SEM of cauliflower structures; e) Drying kinetics with several dissolution-drying cycles.

The size increase of the ‘cauliflowers’ with increasing number of wetting/drying cycles leads to the disappearance of the skin at the surface of the sample (Fig. 3). This crystallisation dynamics has direct repercussions on the drying behaviour as can be seen in Fig. 3e. First, with increasing the number of cycles, the drying kinetics gets closer to the drying kinetics of water. Second, the exponential regime associated with the formation of a

salt ‘skin’ that slowed down the evaporation, disappears completely due to the fact that the skin layer disappears with cycling as discussed above. Third, because the skin layer is subsequently replaced by large cauliflowers, the constant rate period extends over a longer period with increasing the number of cycles. The drying dynamics can thus be described as a constant rate period due to the capillary transport to the surface followed by a diffusive regime. The transition between these two regimes becomes smaller and smaller with subsequent cycling.

Deliquescence-drying experiments: If water vapour is introduced into the porous medium, a very different recrystallisation dynamic is observed. The experiments show that the formation of large cauliflower crystals due to secondary nucleation upon recrystallisation is almost completely absent with increasing the number of cycles (Fig. 4a and Fig. 4b). The deliquescence of the salt crystals is a slow process which leads to the formation of a very homogeneous salt solution which gradually invades the porous network of the stone, thus transporting the salt to the interior of the stone. The subsequent recrystallisation (as a primary nucleation) of the homogeneous salt solution leads to the increase of the number of large cubic crystals (Fig. 4c); their formation is usual for recrystallisation because at each cycle impurities are expelled (Shahidzadeh and Desarnaud, 2012).

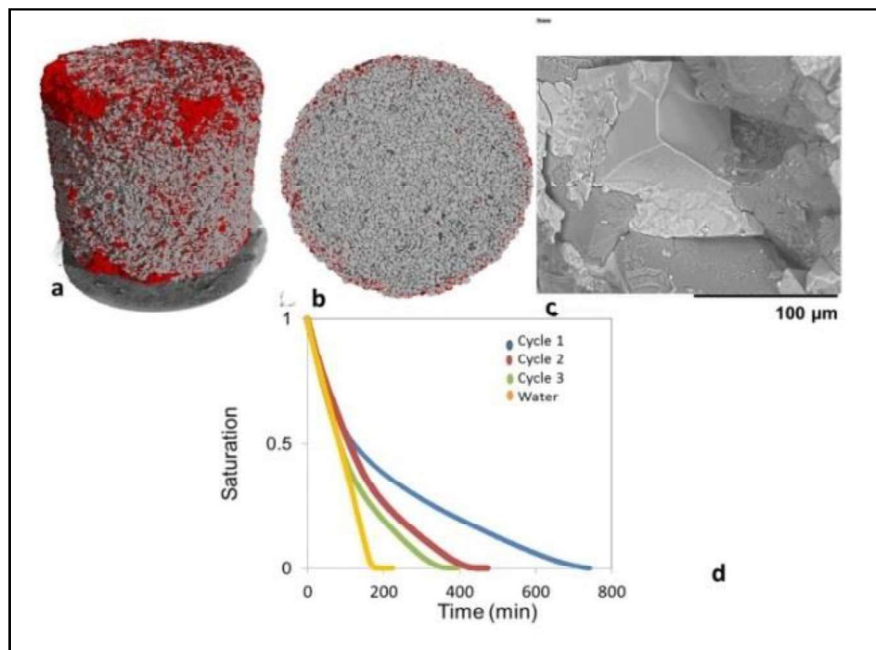


Fig. 4: Recrystallisation due to several deliquescence-drying cycles at RH~20%; a and b) X-ray μ -CT analysis, showing salt crystals (red) on and beneath the surface; c) SEM picture of large a cubic crystal in between the grains at the subsurface after 3 cycles of deliquescence-drying; d) Drying kinetics with several deliquescence-drying cycles.

The supersaturations is very high (Desarnaud and Shahidzadeh-Bonn, 2011) and the increase of salt concentration in the solution before recrystallisation reduces the wetting properties of the solution which in turn at high evaporation rates can be the cause of the retraction of the solution into the porous network and the crystallisation in the subsurface as is clearly visible in the microtomography images (Fig. 4b).

3.2. Microscale experiments

To confirm this hypothesis, we did some experiments in single square microcapillaries (100 μ m) to represent a single pore in a porous network. The results confirm that with an increasing number of cycles of deliquescence-drying, there is a retraction of the salt solution inside of the pore due to the increase of concentration and the formation of more cubic crystals. As it can be seen in Fig. 5, at the first cycle crystallisation occurs at the entrance of the capillary with the formation of a layer blocking the entrance. With two deliquescence-drying cycles, first the skin at the entrance is gradually replaced by well-shaped cubic crystals at the outer wall of the microcapillary and a second part of the salt solution retracts inside of the capillary leading to a deeper crystallisation in the microcapillary (Fig. 5b). In the dissolution-drying experiment, the salt crystallizes outside the microcapillary as efflorescence, and its quantity increases with the number of cycles (Fig. 5c) which is in good agreement with the bigger Cauliflowers efflorescence found in the sandstone experiments.

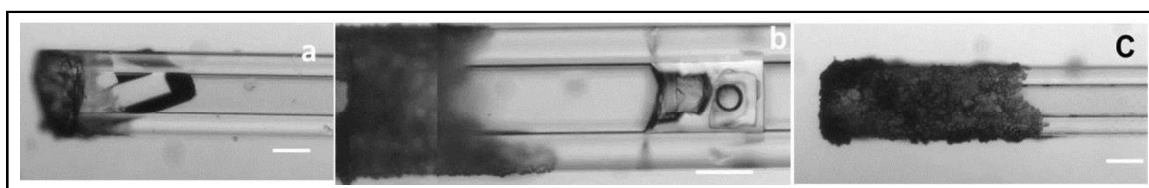


Fig. 5: a) crystallisation of NaCl after first drying; b) Crystallisation after 3 deliquescence-drying cycles; c) after 3 dissolution-drying cycles, in 100 μ m square micro capillaries.

The way of salt crystallisation is a key factor for understanding the crystallisation not only for NaCl. In previous experiment we have shown that for Na₂SO₄, the deliquescence-drying cycles (long process) leads to the primary nucleation and growth of anhydrous crystals (thenardite) occurs (Desarnaud *et al.*, 2012) (Figures 6a and 6b). The homogeneous sodium sulfate solution can reach high concentration during long evaporation without any nucleation, favoring the formation of isolated thenardite crystals which leads to no damage. On the other hand, during rewetting of dissolution-drying experiment (very rapid process) in microcapillaries loaded with Na₂SO₄, anhydrous microcrystals dissolve only partially, giving rise to a heterogeneous salt solution that is supersaturated with respect to the hydrated phase. The remaining anhydrous crystals then act as seeds for the formation of large amounts of hydrated crystals, creating grape-like structures that expand rapidly (Figures 6a and 6c). These clusters can generate stresses larger than the tensile strength of the stone, leading to damage.

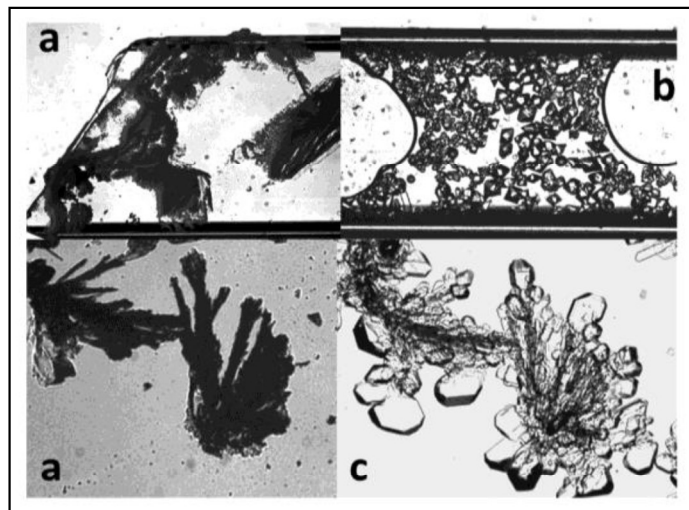


Fig. 6: a) After totale evaporation of Na_2SO_4 solution in capillary (C1) formation of anhydrous crystal (thenardite); b) Crystallisation primaire of thenardite after 3 deliquescence-drying cycles; c) rewetting of the dissolution-drying cycles: formation of clusters due to the growth of hydrated crystals on the remaining thenardite microcrystallites.

4. Conclusion

This paper summarized experimental studies showing the major role played by different salt crystallisation pathways on the drying behaviour of salt-containing sandstones subjected to several wetting-drying cycles. We show that the kinetics of crystal growth due to primary or secondary nucleation are of key factors for understanding the drying behaviour of salt contaminated porous materials and the possible physical weathering generated by salt crystallisation. We provide a clear identification of the different probable regimes that are possible, depending also on external parameters such as the relative humidity.

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