Exploring the crystallization and dissolution behavior of NaCl

S. Godts[1,2,3], M. Steiger[4], J. Desarnaud[1,5], S. A. Orr[6], V. Cnudde[3,7], H. De Clercq[1] and T. De Kock[2]

[1] *Royal Institute for Cultural Heritage (KIK-IRPA), Monuments Lab, sebastiaan.godts@kikirpa.be, Brussels, Belgium*
[2] *Antwerp Cultural Heritage Sciences, ARCHES, University of Antwerp, Belgium*
[3] *Ghent University, Department of Geology, PProGRess, Ghent, Belgium*
[4] *University of Hamburg, Department of Chemistry, Hamburg, Germany*
[5] *Belgium Building Research Institute (BBRI), Renovation & Heritage Lab, Brussels, Belgium*
[6] *University College London, Institute for Sustainable Heritage, London, United Kingdom*
[7] *Utrecht University, Department of Earth Sciences, Utrecht, The Netherlands*

Extended abstract

As part of a research project(*) investigating phase transitions of commonly found salt mixtures in the built environment, initial experiments were carried out with NaCl to define the experimental procedure. Results of these experiments include the crystallization and dissolution behavior and are presented. The behavior was recorded via time-lapse imaging (HIROX) under specific relative humidity (RH) changes produced by a relative humidity generator (GenRH(*)) coupled to a small windowed chamber (Mcell). The experiments started with 0.5µl droplets on a glass slide imaged at a magnification of 50 and 100 (respective resolutions 3.79 and 1.90 µm). The solution concentration of each droplet is initially 4 mol kg^{-1}, theoretically decreasing to 1.51 mol kg^{-1} (at 293.15 K) at 95% RH.

Three experiments were carried out with unconfined droplets conditioned under diverse RH changes. For **exp1** the RH moves down in steps of 5% after 60 min and remains at the target for 60 min before moving back to 95% for 60 min (partly shown in fig.1, green line). All RH steps between 95 and 15% were carried out considering the above example. For e**xp2** and **exp3** the RH moves continuously between 95 and 15 in steps of 5%, with respective time steps of 5 and 60 min (fig. 1, blue and yellow lines). The 60 min steps in **exp3** were limited to 5% above and below the RH_{eq}.

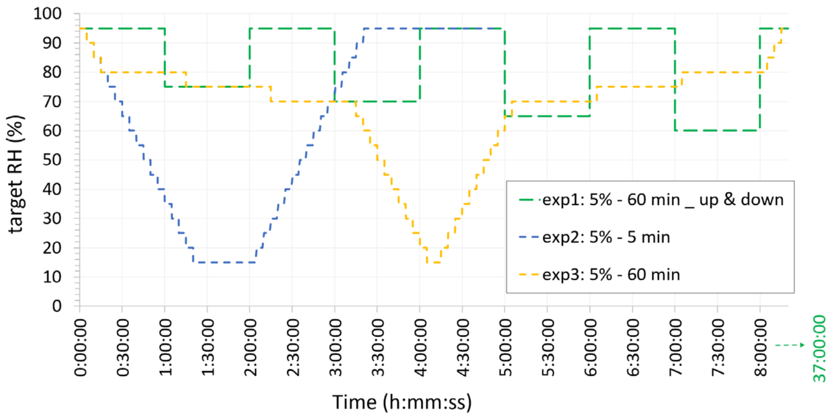

FIG. 1. Visualization of the experimental procedures (**exp1, 2 and 3**) (temperature: 293.15 K (±1))

To determine the crystallization and dissolution behavior several time intervals are defined as:

- **t_1 :** the time the equipment needs to reach the RH_{eq} (75.3% at 293.15 K).
- **t_2 :** the time when the equipment reaches the RH_{eq} until the first visible crystal or surface wetting, which can be considered as the induction time.
- **t_3 :** the time for the crystals or solution to fully grow or dissolve, thus the effective growth/dissolution times (not to be confused with growth rate).
- **$t_4 = t_2 + t_3$** (the total time when the equipment reaches the RH_{eq} until the end of visible growth/dissolution).
- **$t_5 = t_1 + t_4$** (the total experimental time).

Figure 2 shows an example of several time-lapse images at specific experimental intervals and illustrates that the effective growth time (**t_3**) is the time recorded between images (**b)** and (**d**), thus including the final crystallization of the liquid film.

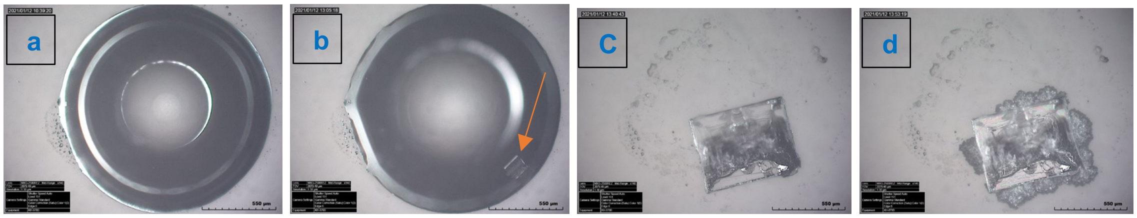

FIG. 2. Example of time-lapse images at defining intervals when decreasing the RH in steps of 5% each 60 min. **(a)** situation of the solution at 95% RH after 60 min; **(b)** the onset of nucleation at 70% RH (exaggerated to visualize the crystal); **(c)** the main crystal is completely crystallized at 70% RH; **(d)** the remaining liquid film under the main crystal is crystallized at 70% RH.

When considering **t_3**, the results of **exp1** confirm previous studies in which crystallization is faster than dissolution. However, when the solution is conditioned at 95% for 60 min followed by a decrease to 75 and 70% the droplet size reduces but no crystal is formed, while at 65% a small crystal is formed just before it returns to solution at 95%. At 60% the crystal growth is almost complete after 47 min while complete dissolution takes 40 min (±0.5), thus crystallization takes more time compared to dissolution. Decreasing the RH further significantly reduces the crystallization time (**t_3**), while dissolution remains similar throughout the experiment with an average time of 45 min (±3). Things become even more interesting when looking at time **t_4** in the same experiment. For example, crystallization takes more time compared to dissolution (respectively 51 and 42 min ±0.5) when moving from 95% down to 55%. In **exp2** and **exp3** a wide time difference is derived between crystallization times (**t_3**) with on average 13 and 41 min, which can be explained by the slower evaporation of the droplet when conditioned at a RH closer to the RH_{eq}. More specifically, in **exp2** when the RH moves down 5% each 5 min the first crystal was observed when the equipment reached 56% and complete crystallization at 43%, while both are observed at 70% in **exp3**. A similar conclusion was derived from the dissolution times (**t_4**) with 41 and 109 min for respectively **exp2** and **3**.

The results show important behavioral aspects when considering crystallization events in realistic environments. With the data demonstrating how crystallization can take longer than dissolution, when conditioned for 60 min, as far as 20% below the RH_{eq}. In the use of climate data for risk assessment both crystallization and dissolution processes are deterministic time steps to consider. Also, the gradient of changes in RH, the minimum and maximum within a cycle, strongly affect crystallization/dissolution times and should therefore be taken into account. The importance of considering salt kinetics when estimating the number of crystallization cycles in a given environment is also influenced by factors such as the exposed surface area of crystals/solution (unconfined versus confined), the behavior of a single salt versus mixture, the resolution and location of climate measurements. Further research on the subject can aid model parametrization and the prediction of the damage potential of salts in porous media. Next steps in this research project include the determination of relevant RH thresholds for commonly found salt mixtures.

(*) Project and acknowledgments: BRAIN 2.0 joint PhD project (PREDICT), Phase Transitions of Salts under Changing Climatic Conditions, funded by the Belgium Science Policy (Belspo). The authors further acknowledge "BOF, project UG_2832369580", "JPI-JHEP project KISADAMA" and "FWO Research Grant 1521815N" for the GenRH humidity generator.