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Dissolution and deliquescence/crystallization cycles: Importance of the kinetics of crystallization

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We have studied the impact of the crystallization dynamics for the two salts Na2SO4 and NaCl on damage during wetting/drying and humidity cycling. There are in general two ways in which the salt, once crystallized, can take up water again: by bringing it in contact with liquid water (dissolution) or water vapour (deliquescence). Here, We show the importance of the kinetics of crystallization at microscopic scale and the interfacial properties of the salt solutions and crystals on the damage observed at macroscopic scale.

We investigate crystallization of Na2SO4 and NaCl after wetting with water and during either drying cycles or humidity cycling. We do this both at macroscopic scale (in sandstones) and on a microscopic scale, studying crystallization growth under the microscope. Under the microscope, using direct imaging we investigate the kinectics of dissolution in contact with liquid water and deliquescence in contact with water vapor followed by crystallization during the evaporation; we do so for both salts. Experiments were done in unconfined (drop evaporation) or confined (square microcapillaries) geometries having different wetting properties (hydrophilic and hydrophpbic), to asses the effects of confinement and wetting.

Sodium sulphate has both hydrated and anhydrous forms and we show that the different solubilities of these two phases can lead to severe damage in the sandstone during rapid rewetting with water followed by drying. The microscopy studies show that this happens because of the only partial dissolution of anhydrous crystals upon rewetting, leading to the very rapid formation of clusters of hydrated crystals on anhydrous crystals which act as nucleation sites. The large volume change that is concomitant with the formation of these clusters generates stresses in the material that are larger than tensile strength of the stone. These phenomena are absent in salts such as sodium chloride with one crystalline phase. In accordance with this, we see that these lead to less damage under the same conditions of rewetting/ drying .

On the other hand, we show that humidity cycling which provokes slow deliquescence followed by recrystallization can inverse this situation: there can be more damage for sodium chloride due to a faster crystallization growth with higher crystallization pressure during repeated humidity cycling. For sodium sulphate, our experiments reveal a slow but complete deliquescence that leads to the direct formation of isolated anhydrous crystals. The crystallization of the anhydrous form generates very small stresses that hardly or not damage the materials during repeated cycles similar to those of rewetting/ drying.

These results shed some light for on how the kinetics pathway of crystallization of NaCl and Na2SO4 plays an important role on the way these salts cause damage under different environmental conditions. This opens the way to a better understanding of salt damage by these two important salts, but also suggests how to best desalinate contaminated stones depending on the nature of the salt.