

# Moisture sorption behaviour of salt mixtures in porous stone

Christoph Franzen\*, Peter W. Mirwald

*Institut für Mineralogie & Petrographie, Leopold-Franzens-Universität Innsbruck, Innrain 52, A-6020 Innsbruck, Austria*

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## Abstract

Moisture in stone material is the key factor for all stone deterioration processes and also in weathering of cultural heritage. With additional presence of salts in the material the situation gets even more critical. While the properties of pure salts with moisture are well known, knowledge about the interaction of salt mixtures with moisture is still poor. In different approaches the reactions of salt-contaminated stone material on changing moisture were tested in the laboratory. Experiments with different solutions in the Na–Mg–SO<sub>4</sub>–NO<sub>3</sub>–H<sub>2</sub>O system revealed interesting new results on the moisture behaviour of salt-contaminated samples. Theoretical considerations and computer simulations are helpful to interpret the data obtained, but are not yet sufficient to explain the real processes acting on site at the monuments. More encouraging to this fact are complementary studies on visible efflorescences in the same salt system. It is shown how by experimental approaches the understanding on salt-induced stone deterioration is strongly complemented.

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## 1. Introduction

Deterioration of porous structured building material such as stone, brick, ceramics and concrete due to salts has been identified as a major process in cultural heritage weathering and natural erosion since several decades (Schmölzer, 1936; Arnold, 1981; Goudie and Viles, 1997). Reported case studies are numerous (Doehne, 2002), underlining the overall importance of the matter and revealing the strong need for much more scientific attention. All kinds of soluble

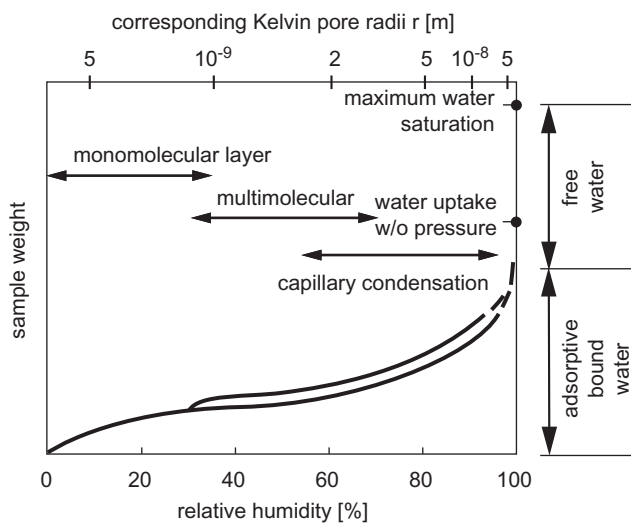
salts can be identified in different positions and locations of world's architectural heritage (Arnold, 1981). Conclusive explanations of the whole salt-related processes fail at the complexity of the problem. As the main agents the cations of sodium, potassium, calcium and magnesium are generally detected. Their anionic counterparts are sulphate, nitrate and chloride. In the understanding of the essential processes which are supposed to happen in the pore space, significant achievements e.g. related to crystal pressure were recently reported by Steiger (2005). The salts are most often readily water soluble and transported in the porous stone material by water. Due to fractionation and accumulation in cyclic processes, high salt contents are generated in the stones and may distribute in different positions (Arnold et al., 1989). Furthermore, the salts are not only driven by fluid water. Some salts interfere highly with water

\*Corresponding author. Present address: Institut für Diagnostik und Konservierung an Denkmälern in Sachsen und Sachsen-Anhalt e. V., Schloßplatz 1, 01067 Dresden, Germany. Tel.: +49 351 48430 410, +43 512 507 5500; fax: +49 351 48430 468, +43 512 507 2926.

E-mail addresses: [franzen@idk-info.de](mailto:franzen@idk-info.de) (C. Franzen), [peter.mirwald@uibk.ac.at](mailto:peter.mirwald@uibk.ac.at) (P.W. Mirwald).

from atmospheric humidity. The phenomenon of wet-looking facade parts on monuments is well known and related to contamination with hygroscopic salts within the pore space of those parts. The correlation of the monitoring of climate to the monitoring of the salt efflorescences does give indications for conservation approaches (Laue, 2005). In some cases, rather than salt removal one may take the opportunity to decelerate the salt-related deterioration by regulation of the climate (Bläuer Böhm et al., 2001). However, to get better understanding of the water–salt interaction in the pores, the first approaches referred to the thermodynamics of the pure salts which are very well known and can be checked in standard chemical literature. Immediately it became obvious that these specifications are not sufficient to explain the effects which are documented on the monuments (Arnold et al., 1991). The quite different behaviour of salt mixture systems compared to the pure salt systems was pointed out by Steiger and Zeunert (1996) in experiments and model calculations. The calculated model diagrams give best basis to evaluate the data of salt mixture systems. But the application and transmission of such models into study cases on real objects is still scarce.

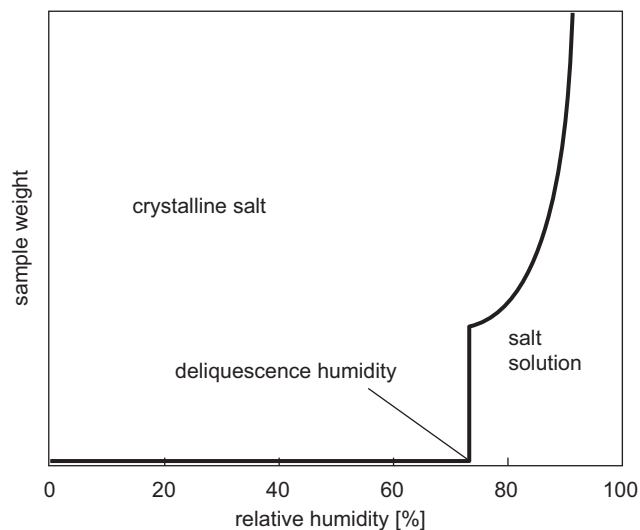
Moreover, the implication of atmospheric humidity on the processes in deterioration of porous material is still often underestimated. Not only with its visible outer surface but also with its total through-the-pores-accessible surface a porous material is in contact with the atmosphere and thus open to the moisture. Water molecules are taken up or are released as a function of changes in air humidity. The equilibrium state function of typical building material gives an S-shaped curve of sorption isotherm as shown in Fig. 1. Some interpretation of the hygric processes occurring in porous material



**Fig. 1.** Sketch of isotherm for water sorption in porous material, modified after Kiessl (1983).

is also given in the scheme. The material moisture is elevated with rising humidity. In low humidity a monomolecular layer of  $H_2O$  is built up. If humidity exceeds some 33%, multimolecular layers are formed. At humidity even higher than 50% relative humidity (r.h.) capillary condensation becomes a relevant process. Pores with pore radii larger than  $2\ \mu\text{m}$  are successively filled. With respect to its enormous capacity the r.h. is a highly buffered parameter. Thus, r.h. is the determining force for the material moisture. As the relative humidity continuously changes during daytime, the equilibrium between atmospheric moisture and material moisture is seldom reached. The sorption and desorption interaction processes happen within minutes and several cycles can be observed in one day (Franzen and Mirwald, 2004).

The sorption curve for single salts is schematically given in Fig. 2. Physically solely the surfaces of the salt crystals interact with humidity. At a certain point of r.h. dissolution of the salt in water occurs. Chemically here a saturated salt solution coexists with salt crystals and the so-called deliquescence humidity. The deliquescence humidity, most often given as r.h. value, is the water vapour pressure in air, which is in equilibrium with the (over-)saturated solution of the given salt. With elevated humidity the salt solution becomes diluted. A typical example for such a system is NaCl. Deliquescence humidity for NaCl is 75% r.h. A salt including hydrated crystal phases is e.g. the highly deteriorative  $NaSO_4 \cdot nH_2O$ -system. The sorption curve for such a system is given in Fig. 3. Also there is no significant water uptake below the deliquescence humidity. If the surrounding atmospheric humidity covers the stability field of the hydrate, the sample weight is increased due to its formation. When humidity



**Fig. 2.** Weight change due to dissolution above deliquescence humidity for simple salts on the example of NaCl, modified after Price (2000).

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