

# Abstract

It is widely accepted that phase transitions of salts are the major cause of damage to porous materials such as stone, brick and mortar. Stress is generated in these materials by crystals growing from supersaturated solutions (crystallization pressure) and during hydration reactions (hydration pressure). In order to understand the underlying processes, the experimental observation of phase transition reactions within pores and their thermodynamic modeling are highly desirable. In the present thesis X-ray diffractometry under controlled conditions of relative humidity (*RH*) and temperature (RH-XRD) was applied for the in situ investigation of such reactions. The Pitzer ion interaction model was used to construct the phase diagrams and to predict appropriate experimental conditions.

RH-XRD measurements were carried out with bulk samples of salts and within the confined spaces of a porous material. It turned out that the kinetics of phase transition reactions depends strongly on the ambient relative humidity. A new extrapolation method was applied to determine equilibrium humidities of phase transition reactions from rate measurements at different values of RH. The method, which offers accurate and precise results, was also successfully applied to phase transitions in confined spaces of porous substrates. Glass frits with different nominal pore sizes were selected as porous substrates, because the amorphous material did not interfere with the X-ray patterns of the salt phases. The median pore sizes of the selected glass frits, in the range of 1.4–70  $\mu\text{m}$ , are typical for many building materials such as natural stone and brick. The equilibrium humidities were neither affected by crystal size nor by the confinement in the pore space of glass frits. Kinetic measurements revealed that the dynamics of deliquescence–crystallization and hydration–dehydration cycles in porous materials is strongly affected by both frequency and amplitude of the ambient humidity variation. Quite short-term variation of ambient relative humidity, e.g. typical daily fluctuations, might induce damaging cycles within the pore space of building materials.

In the case of the  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ – $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  hydration it was shown that not only the rate but also the mechanism of hydration reactions is affected by the relative humidity. At humidities below the deliquescence humidity of the  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  phase the hydration proceeds as a true solid state reaction and the stress generated during crystal growth is best treated as a hydration pressure. At humidities above the deliquescence humidity, the hydration proceeds as a two-step reaction, involving the dissolution of the  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  forming a supersaturated solution with respect to the  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and the subsequent crystallization of the hydrated phase. The generated pressure is then best treated as crystallization pressure. Of course, it is impossible to observe the appearance of supersaturated solutions with in-situ RH-XRD measurements. But strain measured as mechanical response of the generated

pressure confirmed that the volume expansion during the one step hydration leads to substantial pressure and that the deliquescence–recrystallization pathway is more efficient in generating stress.

Apart from chlorides, nitrates and sulfates, acetates have been identified as a major constituent in salt efflorescences grown on museum artifacts. The triple salt  $\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ , thecotrichite was often found as efflorescent salt on limestone and ceramic objects. In an analytical study efflorescences on seriously damaged Dutch tiles of glazed ceramics of the collection of the Stedelijke Musea in Kortrijk, Belgium, were analyzed and the composition of the remaining salt mixture in the tiles was determined. To improve the understanding of the thecotrichite formation the phase diagram of the quaternary system  $\text{Ca}(\text{CH}_3\text{COO})_2\text{--CaCl}_2\text{--Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$  was constructed using the semi empirical Pitzer ion interaction model. Due to the lack of available experimental data for the ternary system  $\text{Ca}(\text{CH}_3\text{COO})_2\text{--Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$  new solubility measurements had to be carried out. The data were then used to determine the missing parameters required for the treatment of the quaternary system  $\text{Ca}(\text{CH}_3\text{COO})_2\text{--CaCl}_2\text{--Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$ . These interaction parameters and the equilibrium constants of the respective solid phases then allowed for the calculation of the molalities and water activities of saturated solutions of each possible composition. A lot of information on the crystallization and deliquescence properties was derived from the phase diagram and finally the deliquescence and crystallization behavior of a synthetic thecotrichite efflorescence was observed with in-situ RH-XRD measurements. It was found that thecotrichite dissolved completely under formation of  $\text{Ca}_2(\text{CH}_3\text{COO})_3(\text{NO}_3) \cdot 2\text{H}_2\text{O}$  with increasing humidity. In contrast,  $\text{Ca}_2(\text{CH}_3\text{COO})_3(\text{NO}_3) \cdot 2\text{H}_2\text{O}$  dissolved completely with decreasing humidity and thecotrichite crystallized out. Under conditions of increasing RH  $\text{Ca}_2(\text{CH}_3\text{COO})_3(\text{NO}_3) \cdot 2\text{H}_2\text{O}$  crystallization occurred delayed, i.e. at humidities above the calculated equilibrium humidity. It is concluded from mass balance considerations that solutions supersaturated with respect to  $\text{Ca}_2(\text{CH}_3\text{COO})_3(\text{NO}_3) \cdot 2\text{H}_2\text{O}$  are formed under such conditions. This is an important result as crystals growing in pores can only generate pressure if they are in contact with a solution of sufficient supersaturation.

In conclusion, the in-situ RH-XRD investigations carried out in this work provide a significant contribution to a better understanding of salt weathering phenomena. Damaging phase transition reactions were successfully observed within the confined spaces of a porous material for the first time. Finally, the conditions for damaging phase transition reactions of single salts and salt mixtures, which are relevant to the deterioration of building materials or museum artifacts, were determined.