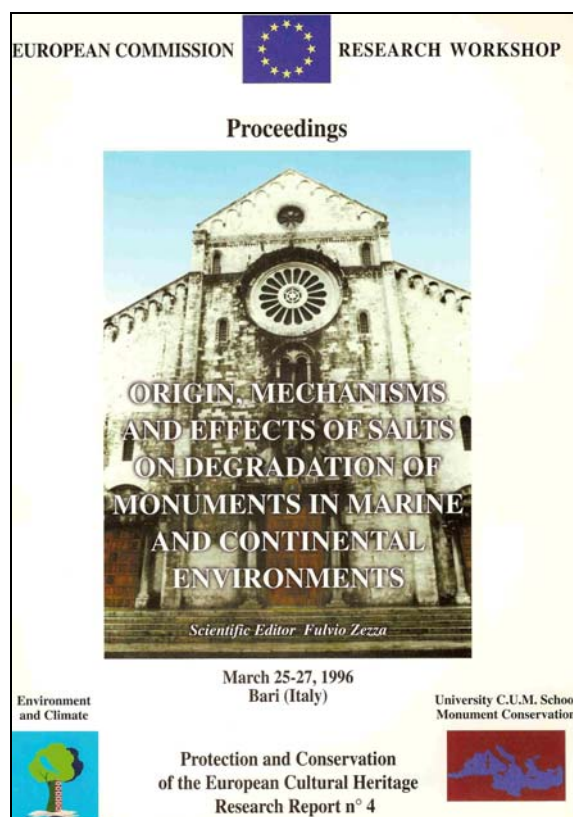


Distribution of Salt Mixtures in a Sandstone Monument: Sources, Transport and Crystallization Properties

Michael Steiger

*Institut für Anorganische und Angewandte Chemie,
Universität Hamburg, Germany*

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M. Steiger

*Institut für Anorganische und Angewandte Chemie,
Universität Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg*

1. Introduction

Salts are a major cause of decay in porous materials such as stone, brick, concrete, etc. Severe damage of these materials results when water evaporates and dissolved salts crystallize. Although there might still be a deficit in our understanding of the nature of the underlying processes, which generate high internal pressures and disruptive stress, the deleterious effects of salt crystallization are well established, both, from laboratory experiments and observations at many monuments as well.

Contributions from different sources and transport as pore solutions followed by enrichment due to evaporation of water are characteristic features of complex salt systems evolving in historic monuments over long periods of time. Depending on the nature of the sources and the type of material salt contaminations usually found in historic monuments comprise of many different ions. Typically the chlorides, nitrates and sulfates of sodium, potassium, magnesium and calcium have to be considered. Depending on the temperature and relative humidity (RH) and the solubilities in such multicomponent mixtures, ions may remain in solution or salts may be precipitated and enriched when water evaporates.

Arnold and Zehnder¹ have extensively studied the evolution of salt systems in historic monuments affected by rising damp. They described how the interaction of the different processes results in the accumulation of salts in a zone approx. 0.5–3 m above ground level, where a characteristic vertical profiling due to fractionated crystallization is observed. The same arguments also apply to the upper parts

of a facade, where deposition from the atmosphere is often found to be the dominant source for the accumulation of salts, mostly sulfates. Transport of salts in those areas is mainly determined by the capillary uptake of rain water, the formation of surface run-off water and subsequent drying. Again, the interaction of the different processes results in characteristic distributions of salts in a wall².

Once that salts are enriched within the pores of stone or any other porous material phase transformations such as crystallization/dissolution, hydration/dehydration or the formation and decomposition of double salts are continuously occurring as a result of temperature and humidity fluctuations of the surrounding environment. These phase transformations are generating the internal pressures responsible for salt damage. The behaviour of a single salt contaminating a porous material can be easily derived from its deliquescence humidity, which is the relative humidity in equilibrium with a saturated solution of the respective salt. At high relative humidities, above the deliquescence humidity, the salt is completely dissolved, at lower relative humidities the salt remains solid. Thus, undesirable dissolution/crystallization cycles do not occur if the ambient humidity does not fluctuate across the deliquescence humidity.

It has been recently shown, however, that this approach does not apply to salt mixtures where phase transformations are continuously occurring within ranges of relative humidity^{3, 4, 5}. The same authors have also dem-

onstrated that, in principle, the behaviour of salt mixtures can be analysed using a chemical equilibrium model based on the approach of Pitzer⁶.

This paper presents a case study of the salt contamination in a historic sandstone monument. The analytical data obtained from the chemical analysis of drillcores are interpreted with respect to the sources and transport processes determining the distribution and composition of the salt mixture found in the wall. The same thermodynamic model that has been previously used^{4,5} is now applied to the experimental data to analyse the hygroscopic and crystallization properties of the salt system.

2. Methods

The north facade of the former convent of Birkenfeld (Northern Bavaria, Germany) founded in the 13th century has been subject to a detailed investigation of concentration and distribution of salts. The building is mainly built of a sandstone rich in clay minerals and feldspar (Schilfsandstein, upper triassic). This sandstone is known to show only poor weathering resistance. It is quite susceptible to salts and moisture. In an earlier study⁷ large accumulations of salts have been found in the base of the south wall. In accordance with these findings the mapping of weathering forms at the same wall⁸ also revealed that crumbling, flaking and the formation of scales are most pronounced in the base.

Salt contamination had to be also expected when planning the investigation of the north facade. Five drillcores (diameter: 18 mm) have therefore been taken in different heights from 0.65–5.2 m above ground level. In addition, two drillcores from the interior side of the same wall and one drillcore from the south facade have been analysed. The drillcores have been cut into slices of approximately 3 mm near the weathering surface and into 15 – 20 mm pieces in greater

depth. The total lengths of the drillcores have been about 100 mm.

All of the samples obtained in this way were homogenized by grinding to grain sizes <120 μm and subsequently extracted with deionized, bidistilled water (500 mg sample, 25 ml water). The aqueous suspensions obtained were filtered and analysed using ion chromatography (sulfate, nitrate, chloride), atomic spectrometry (sodium, potassium, magnesium, calcium) and photometry (ammonium).

3. Results and discussion

The analytical results confirmed that the base of the north facade of the building is also contaminated with salts. Large concentrations of nitrate, potassium and magnesium have been found. These ions showed pronounced vertical profiles with maximum enrichment at heights of approximately 2–3 m. Their concentrations show only small variations with depth. As an example, the nitrate distribution is presented in Fig. 1. The distributions of sodium, chloride and ammonium are closely matching that of nitrate, their concentrations are much smaller, however.

The sulfate distribution in the wall, is completely different. Strong horizontal concentration gradients can be seen from Fig. 1. The vertical profile is characterized by a shift of the maximum concentrations. Below 2 m maximum concentrations of 2 w.% are found at the stone surface. Penetration to greater depths is observed above 2–3 m. Most of the sulfate is balanced by calcium as the counterion indicating the presence of sparingly soluble calcium sulfate minerals, probably gypsum. Only the drillcores taken above 3 m revealed an excess of sulfate vs. calcium indicating significant contributions of sulfate to the hygroscopic fraction of the salt system.

The salt distributions found can be interpreted as the additive effect of two different sources. The distributions of nitrate, po-

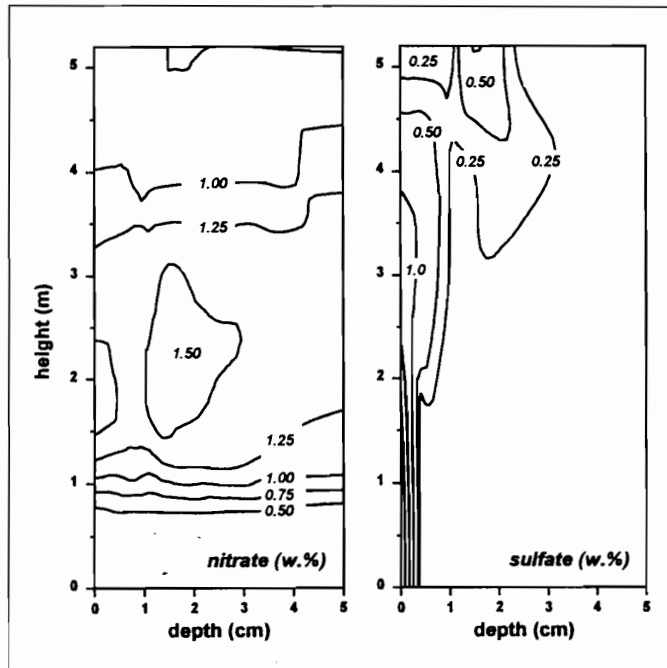


Fig. 1 Distribution of nitrate and sulfate.

tassium and magnesium (also sodium and chloride) can be regarded as being the result of the input of these ions by rising damp.

The zone of maximum enrichment reflects the height of capillary rise of water. Fractionation during the vertical transport is indicated by a shift of the K/Mg ratio, which is significantly higher below the accumulation zone.

On the other hand, the sulfate distribution in the wall indicates that deposition of sulfur dioxide from the atmosphere is the main source of sulfate enrichment. This is also confirmed by the analysis of the indoor drillcores yielding sulfate concentrations approximately an order of magnitude lower than outside. In contrast, the nitrate concentrations are practically identical at both sides of the wall. Finally, the integral sulfate concentrations were calculated up to a depth of 100 mm. The values of 12–43 mg/cm² compare well to those determined at other sandstone monuments also exposed to moderate sulfur dioxide pollution.

To study the crystallization properties of

the salt mixture in the wall the chemical equilibrium model mentioned above has been used. For that purpose the concentrations of the ions in the area of maximum salt enrichment at a height of 3 m have been used as input data. The ionic balances indicated that, within experimental uncertainties, sulfate is completely balanced by calcium at that height. Due to the low solubility of calcium sulfate it can therefore be assumed that practically all of the sulfate and calcium ions remain in solid form (gypsum) at all times. Thus, the influence of calcium and sulfate ions on the properties of the hygroscopic salt fraction can be neglected and the hygroscopic salt fraction can be treated as a mixture of magnesium, potassium, sodium, nitrate and chloride, only. Using the concentrations of these ions as input data the crystallization properties at 25°C have been calculated. The results are summarized in Fig. 2, which shows the amount of crystalline salts as a function of the relative humidity.

It can be seen that niter (KNO₃) is the first solid to be precipitated from the salt mixture. The crystallization starts if the rela-

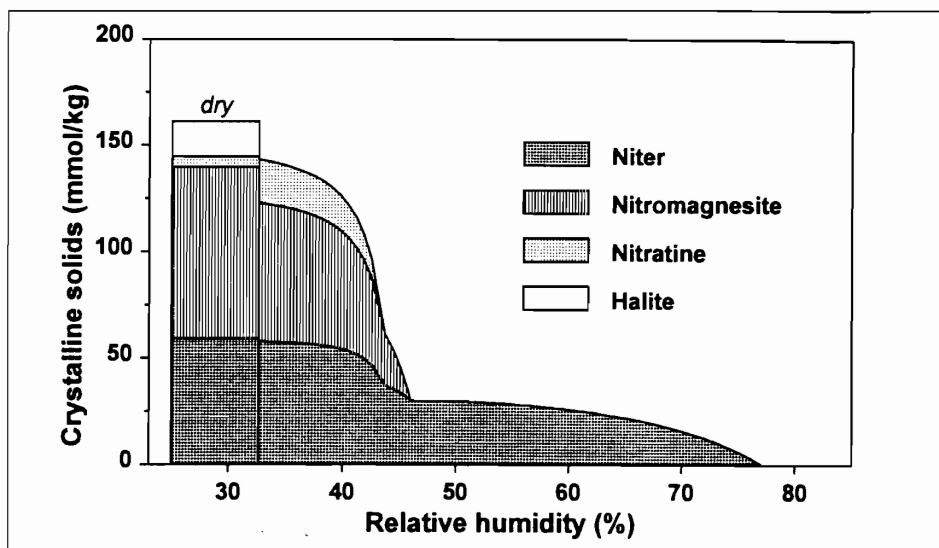


Fig. 2 Crystallization sequences at 25°C (height: 3m, depth: 0–0.3 cm)

tive humidity drops below 77% which is considerably lower than the saturation humidity of pure potassium nitrate (92.7%). Fluctuations of the relative humidity within a range from 47% to 77% cause continuous crystallization and redissolution of niter. Thus, at humidities above 47% all of the sodium, magnesium and chloride and part of the nitrate and potassium ions remain in solution. Decreasing the relative humidity to values below 47% causes the simultaneous crystallization of niter and nitromagnesite ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and, in addition, below 44% nitratine (NaNO_3) starts to crystallize out. Finally the crystallization end-point is reached at only 32.7% relative humidity with the additional crystallization of halite (NaCl). Thus, after complete evaporation of water there remain four different solids, niter, nitratine, nitromagnesite and halite, respectively.

With respect to salt damage it can be concluded that cyclic variation of the relative humidity across a range of about 44%–47% is critical because a large fraction of the salt mixture in the wall is subject to crystallization cycles and severe damage has to be expected. Fluctuations of the relative humidity between 47% and 77% also causes crystallization cycles, involving only potassium ni-

trate, however. Since the amount of niter precipitated is rather small compared to the total concentration of hygroscopic salts (about 0.3 weight percent KNO_3 at 47% relative humidity) salt damage caused by humidity fluctuations above 47% is expected to be less severe. Finally, no salt crystallization occurs at relative humidities above 77%.

Additional calculations have been carried out to determine the influence of the salt mixtures on the moisture content of the stones. The results are shown in Fig. 3. Above 44% relative humidity the salt mixture picks up a significant amount of water. The moisture content strongly increases at humidities above 70%–75% and, finally, at a relative humidity of 89% the saturation value of the sandstone is reached (6.4 w.% of water) which means that the available pore space is completely filled with a salt solution. Due to the swelling and shrinking of the clay minerals the sandstone used at Birkenfeld Convent is very sensitive to large moisture variations. It can be seen from Fig. 3 that the hygroscopic salt mixture might therefore be also responsible for additional mechanical stress at rather high relative humidities where the salts are completely dissolved and no crystallization occurs.

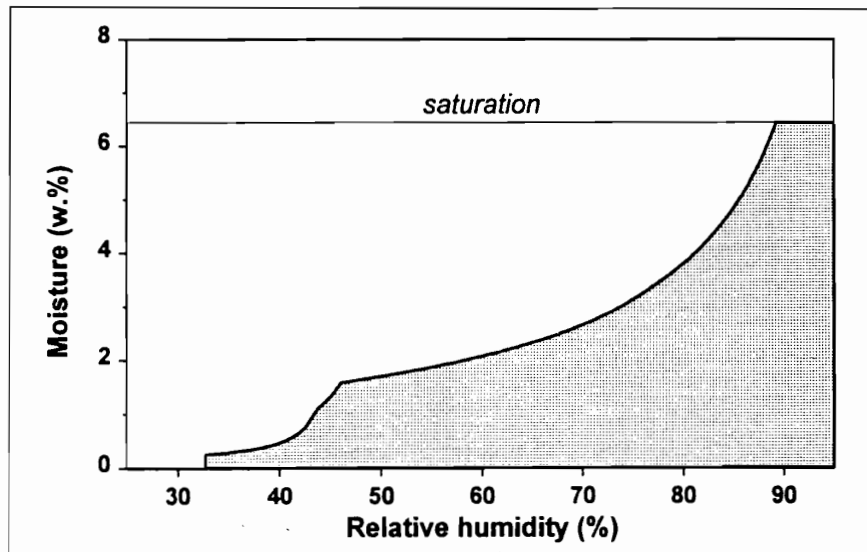


Fig. 3 Hygroscopic moisture at 25°C (height: 3 m, depth: 0–0.3 cm)

4. Conclusions

The analytical results of the ion concentrations in the northern wall of Birkenfeld Convent confirmed that the base of the wall is strongly contaminated with salts. The analysis of vertical and depth profiles of the salt concentrations has shown that input with rising damp is the main source of nitrate, chloride, magnesium, potassium and nitrate. Dry deposition of SO_2 is the dominant source of sulfate in the wall. Most of the sulfate found is balanced by calcium as the counter-ion indicating the presence of sparingly soluble gypsum. Therefore, the salt system in the wall can be characterized as a mixture of two fractions, a hygroscopic salt fraction which is subjected to cyclic dissolution and crystallization and gypsum most of which remains in solid form at all times.

It follows from the analysis of the crystallization properties of the hygroscopic salt mixture in the zone of maximum salt enrichment at a height of 3 m that, under normal outdoor climatic conditions, only a rather small amount of niter (KNO_3) would be subject to crystallization/dissolution cycles. Other salts would probably remain in solution at all times (see Fig. 2). The rate of damage due to salt crystallization alone is therefore expected to be

moderate. The situation becomes different, however, for the indoor environment where the climatic conditions are largely determined by the kind of usage of a building. At present there are no heating facilities installed and the low relative humidities required to cause the crystallization of the main fraction of the hygroscopic salts are hardly ever occurring. It follows that the walls are moist at all times which might promote other undesirable processes (e.g. growth of microorganisms and swelling and shrinking effects). Another usage of the basement, however, as it has been taken into consideration by the owners of the building, would certainly strongly affect the climatic conditions. Heating would probably cause very low relative humidities during winter resulting in the crystallization of a large fraction of the salts present and therefore severe damage has to be expected.

Under normal outdoor climatic conditions the hygroscopic salt fraction is also responsible for large variations in the moisture contents of the wall (see Fig. 3) leading to additional mechanical stress due to swelling and shrinking which is often seen as a major damage process for stones rich in clay minerals as the one used at Birkenfeld Convent⁹. Thus it is expected that both processes, crystallization of

niter and swelling and shrinking of the clay minerals, are responsible for the strong damage observed at the base of the building.

Finally, gypsum, due to its low solubility, does not significantly influence the moisture content of the stone and only a small fraction of the gypsum present will ever be subject to dissolution–crystallization cycles. However, large concentrations of gypsum strongly influence the damage processes discussed so far. Gypsum deposits in the pore space affect the pore size distributions. For example, from the maximum sulfate and calcium concentrations found a gypsum concentration of 2.85 w.% (as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can be calculated. Neglecting the differences in the densities of gypsum and the sandstone this amount corresponds to about 20% by volume of the water accessible pore space. It has been recently shown⁹ that gypsum deposits in the pore space enhance the effect of swelling and shrinking processes and therefore accelerate the damage process. Similar effects of gypsum might also be expected with respect to the crystallization of hygroscopic salts.

It can be concluded that the salt contamination of the wall is largely responsible for the strong damage of the sandstone. The deleterious effects of the salts, however, are to be seen as the combined influence of different processes controlled by both, the crystallization and hygroscopic properties of the salt mixture and the properties of the stone material. Chemical equilibrium models allowing for the prediction of phase behaviour of salt mixtures are very helpful in this respect.

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