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Salt Weathering on Buildings and Stone Sculptures

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Mitigation of salt damages by climate stabilization and salt extractions in the Crypt of St. Maria im Kapitol, Cologne

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ABSTRACT

In 1992-1996 an investigation was carried out to understand the salt damages in the crypt of St. Maria im Kapitol in Cologne: Damages of stones and wallpaintings have been caused by cyclic crystallization and dissolution of the salts halite [NaCl] and nitratine [$NaNO_3$] due to climate changes through heating the crypt. In the crypt the dissolution or crystallisation of halite and nitratine takes place when 65-75% of relative humidity is reached, depending on the thermodynamic properties of the saltmixture halite/nitratine. For ten years the Department of Restoration architects, scientists and restorers have been working together to solve the question, how to diminish the damages and salt concentrations in the crypt. In order to prevent major salt deteriorations in the crypt, the heating system was adapted and the environmental conditions were changed step by step in order to reach values of around 67% relative humidity resulting in a more stable climate and mitigating the deterioration process. A monitoring system was installed to monitor the effects of the climate changes in the crypt.

Keywords: Monitoring, climate stabilization, halite, nitratine, salt extraction

1 INTRODUCTION

Salt weathering on monuments due to climate changes frequently play a major role in the disintegration of various cultural heritages (Arnold & Zehnder 1990; Laue 2005). In general, the crystallization of salts on monuments - accumulated at the surface of a building material - is dependent on environmental conditions. If the relative humidity of the air is lower than the deliquescence humidity of the salt on the surface of a monument, crystallization will occur. If, on the other hand, the relative humidity exceeds the deliquescence humidity the salt remains in solution. Finally, if the deliquescence humidity of a salt falls within the range of variation of the ambient relative humidity, cyclic dissolution and crystallization will accelerate the deterioration of building materials.

Therefore, to preserve a monument it is indispensable to find out and understand the chemical and physical processes damaging the building materials and the conditions under which decay occurs. If it were possible to predict under what climatic conditions a salt will effloresce or hydrate, it would be possible to know which climatic conditions have to be maintained in order to avoid crystallization cycles.

This paper describes a case study of the Crypt of St. Maria im Kapitol in which, after a long investigation period, changes in climate conditions and salt reductions led to a step by step reduction of salt damages.

2 CRYPT OF ST. MARIA OF KAPITOL, COLOGNE

The church St. Maria im Kapitol in Cologne was constructed between 1015 and 1065. The crypt is situated in the eastern part of the church under the choir and about one third to one half of its height is located under ground. The walls of the crypt are built from different kind of building stones, most of them are tuff, trachyte, sandstone and limestone (Laue et al. 1996, Laue 1997). The vaults are adorned by Romanesque wallpaintings.

During their eventful history (table 1) these paintings were covered for an unknown period of time and were finally uncovered around 1900. Their condition at that time is documented by aquarell copies. In the 19th century, between 1838 and 1851, the crypt was used as a salt depot. During the Second World War the crypt was partially destroyed. Thus today, only in the eastern part of the crypt remain original building materials still carrying Romanesque wall paintings in the vaults. In 1969, a floor heating system was installed which was replaced in 1987 by a hot-air heating. In 1976, the walls were partly covered by a restoration plaster, leaving partly visible the original building materials and wallpaintings.

In 1992, extreme damage to the various rocks and plasters was apparent and the crypt was included in a research project in order to understand the crystallization conditions of the salts.

Table 1. Main events of the history of St. Maria im Kapitol

Time	**E**vent
1015 – 1065	Construction of St. Maria im Kapitol
1838 – 1851	Salt depot in the crypt
1945	Destruction during the Second World War
1950 – 1952	Reconstruction of the crypt
1969	Installation of a floor heating system
1977	Covering of the walls by restoration plasters
1987	Changeover to an air controlled heating system (community heating)
1992	Start of the research project to protect the stones and wall paintings

3 ANALYTICAL METHODS

Salt efflorescences were taken from the surface of the building materials and analyzed microscopically, microchemically (Bläuer Böhm 1994) and by using X-ray diffraction analysis. Through aqueous extracts from samples of dry taken drillcores the salt concentration in the walls was determined; for this purpose 100 ml deionized water were mixed with 1 g of sample and filtered. In 1995, the quantitative analyses were executed by a flamephotometer, by atomic absortion spectroscopy, and by photometry. In 2010, quantitative analyses were carried out by electrical conductivity and ion chromatography.

To investigate the question under which climate conditions the crystallizations took place and what kind of damage they are producing, climate measurements were executed combined with the periodic observation of the crystallized salts at defined fields (Laue 2005). First, the climate in the crypt was measured using a recording thermohygrograph while from 2002 a digital datalogger was used permitting to determine under which climatic situation the salts are crystallizing and what kind of damage they are producing.

4 SALTWEATHERING IN THE CRYPT

The degree of the salinity and, therefore, as well the deterioration decreases from the bottom to the top of the walls. Efflorescenses and crusts crystallizing on the surfaces most frequently consist in a mixture of halite [NaCl] and nitratine [$NaNO_3$]. Only to a small degree thenardite [Na_2SO_4], mirabilite [$Na_2SO_4 \cdot 10H_2O$], epsomite [$MgSO_4 \cdot 7H_2O$], gypsum [$CaSO_4 \cdot 2H_2O$] and trona [$Na_3H(CO_3)_2 \cdot 2H_2O$] were analyzed in the crypt (Laue 1995).

The dominance of chlorides was one of the consequences of the utilization of the crypt as a salt depot. Nitrates probably migrated into the walls through ground moisture.

A room climate curve with the averaged daily values for the relative humidity and the temperature is shown for one year in Fig.1. In general, the room temperature varies from about 20°C in summer to about 13°C during the winter months. In the summer months July, August, and September the crypt is quite moist with 70 to 80% of relative humidity. By starting the heating in October, the relative humidity decreases slowly and, during winter, it oscillates around 50%, sometimes in January or February 35% is reached. The dry period continues until April, when the relative humidity rises, so that the crypt becomes quite moist again in July.

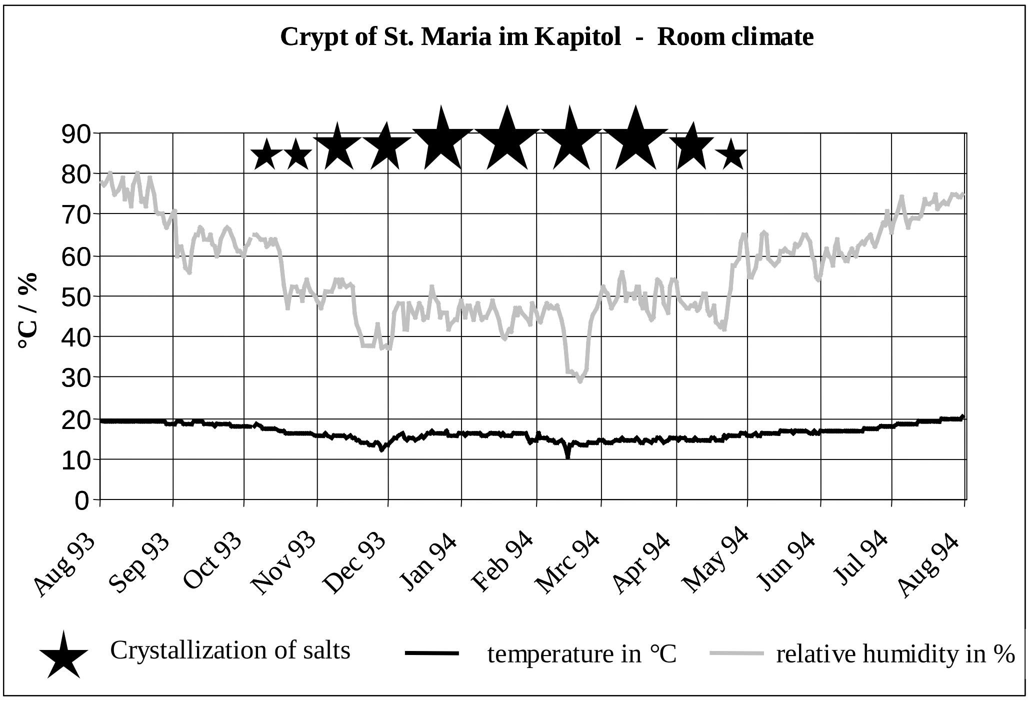

Figure 1. Evolution of the averaged daily values for temperature and relative humidity in the crypt of St. Maria im Kapitol, Cologne related to the observed salt crystallization

After two years of measuring the climate and observing the behaviour of the salts in the crypt, it was possible to predict under which environmental conditions the main salts will effloresce.

In the moist summer months of July, August, and September fluffy efflorescences of halite and nitratine dissolve. At the same time by starting the heating system in October small salt crystals of halite and nitratine begin to grow. More and more salts crystallize until April, when the most damage and decay in the crypt can be observed (see figure 1). In the transitional period around May and June almost no crystallization or dissolution of halite and nitratine is perceptible until July, when the dissolution of the main salts becomes visible again.

The critical relative humidity in the crypt is around 65-70%: above this range halite and nitratine dissolve and below it they crystallize. When exactly this happens could not be determined with the applied measurement equipment.

From laboratory experiments with saturated salt solutions the equilibrium relative humidities of single salts are known (Greenspan 1997) indicating the dissolution or crystallisation of the respective salt. The equilibrium relative humidity of halite is 75.5% and 75.4% of nitratine at 20°C, with temperature variations not particularly influencing the values. Therefore in the crypt the dissolution or crystallisation of halite and nitratine should take place at around 75% relative humidity. But the results of the observation and measurements demonstrate that the equilibrium relative humidity of the salts halite and nitratine is reduced to values of around 65-70% in contrast to the single salts. The reason for this is the different thermodynamic properties of saltmixtures in comparison to the thermodynamic properties of the single salts (Steiger 2005).

In order to prevent strong salt deterioration in the crypt, in 1995 it was suggested to switch off the heating system for one winter period and observe which relative humidity will be reached and how the salt system will react to the changed environmental condition. This suggestion was refused by the proprietor because the crypt of St. Maria im Kapitol was rebuilt with tax funds.

5 MEASURES PREVENTING SALT DAMAGES IN THE CRYPT

Since the investigation in 1995, in the first years until 2000 there were no measures taken in the crypt but further measurements of the salts concentrations in the walls and in the ground were executed complementaryly. These measurements could show that the salt concentration in the walls and in the ground - even in deeper regions of the wall - is so high that salt extraction by poultices alone will not help to reduce the damage in the crypt. Additionally the investigation could demonstrate that the floor is sealed by basalt plates embedded in a cement binder. Therefore water from the ground cannot diffuse from the ground through the floor, but rises up by capillary forces in the porous Romanesque walls accumulating salts near the surface where they cause damages.

In 2000, the damage in the crypt due to salts had risen dramatically. Thus the proprietor (the diocese), the Department of Restoration, the architects, scientists and restorers together were planning a step by step solution in order to diminish the damages in the crypt by having an altogether low financial budget.

Since 2000, the following measures were executed step by step (see table 2):

- In 2000, a professional climate measurement system was installed to get precise and reliable data about the surface temperature, the room temperature, and the relative humidity inside and ouside.
- The floor covering had been opened partly in order to facilitate diffision of liquid from the ground. After two years, in 2004, the floor was covered again with the same basalt plates as before, but now embedded in a pebble bed with open joints to enable evaporation of moisture.
- The restoration plaster applied in 1977 was recovered. Due to the fact that the restoration plaster was applied to the walls together with cement materials, after the recovering of the restoration plaster a higher amount of pores of the walls was available to enable sorption processes in the crypt resulting in a more stable climate.
- Boxes made of wood were installed at the bottom of the walls and pillars in the crypt to initiate a monitoring of the loss of weathered stone material that fell off the walls. In order to find out when and how much the building stone is weathered, the particles pushed off were collected and weighed every two months. In addition, the sample material which fell off could be analyzed indicating the salts which produce the damage respectively.

- Doors and windows in the crypt were sealed up in order to minimize an exchange of humidity to the outdoor climate. The visitors were requested to close the door immediately after they went in and out.
- Finally, an air condition system was installed in order to create a climate in the crypt in which a lower salt activity was expected due to the salt mixture halite and nitratine. The suggested and adjusted value is 67% relative humidty. If the relative humidty is higher than 67% dry air is blown cautiously into the crypt in order to reduce the relative humidity. On the other hand, if the relative humidty is lower than 67% humidifiers moisten the air trying to reach the climate corridor.
- Salt extractions by poultices were executed at defined walls which showed extreme salt deterioration. At first, the areas were brushed slightly before applying poultices which consist just of cellulose. In order to optimize the desalination process poultice desalination consisted of three cycles. In the first and second cycle the wet poultice was applied for 72 hours on the surface; the poultice was kept moist before it was taken off. In contrast to this, in the third cycle the poultice dried for 10 days before it was taken off supporting the crystallization of remaining salts into the poultice.

Table 2. Measures in the crypt since 2000

Year	Measure
2000	Start of periodical monitoring of the damages Start of regular climate measurements Opening of the floor cover Installation of two humidifiers to rise up the relative humidity
2001	First salt reductions by poultices
2003	Sealing of doors and windows Modification of the environmental condition through controlled ventilation
2004	Recovering of the restoration plaster from 1977 Covering the floor again with plates in a pebble bed and with open joints Salt extractions on defined areas
2005	Modification of the environmental condition again by using four humidifiers to further increase the relative humidity Salt extractions on defined areas
2006	Salt extractions on defined areas
2007	Salt extractions on defined areas
2008	Salt extractions on defined areas
2009	Salt extractions on defined areas
2010	Salt extractions on defined areas

6 RESULTS AND DISCUSSION

After about ten years of measurements in the crypt to mitigate the salt damages, the results can be seen in the figures 2 and 3.

Figure 2 demonstrates the evolution of loss of stone material, which fell off from the walls. In 2004, no measurements could be conducted for several months because of the recovering of the restoration render during that time. As a summary, a distinct reduction of the loss can be observed since 2006, when the measures of environmental control and salt extractions began to take effect. Since 2008, the loss of material has been low, except in the months of March and April after heating the crypt for around six months during the winter. In the winter months of

January until March the relative humidity still decreased below 67% (figure 3), although four humidifiers are working. Consequently, the salts halite and nitratine crystallize and cause damage due to the fact that the saturation humidities of the salt mixture is between 67-74% depending on the composition of the mixtures (Steiger 2005). Thus, the most damage can be observed at the end of winter leading still to a loss of stone material in March and April of each year (figure 2).

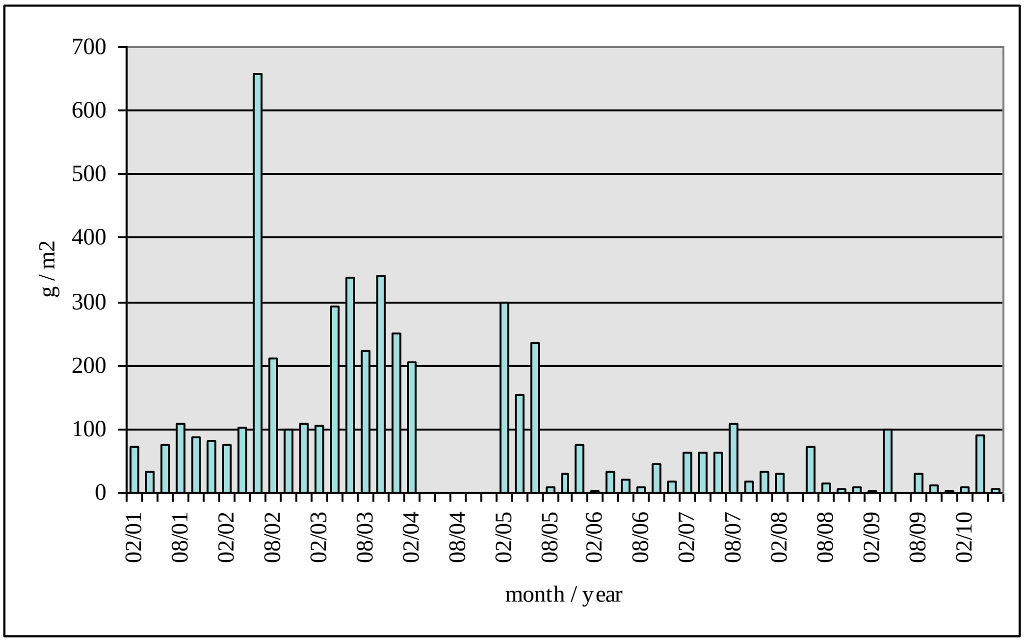

Figure 2. Loss of stone material due to salt weathering in the crypt of St. Maria im Kapitol

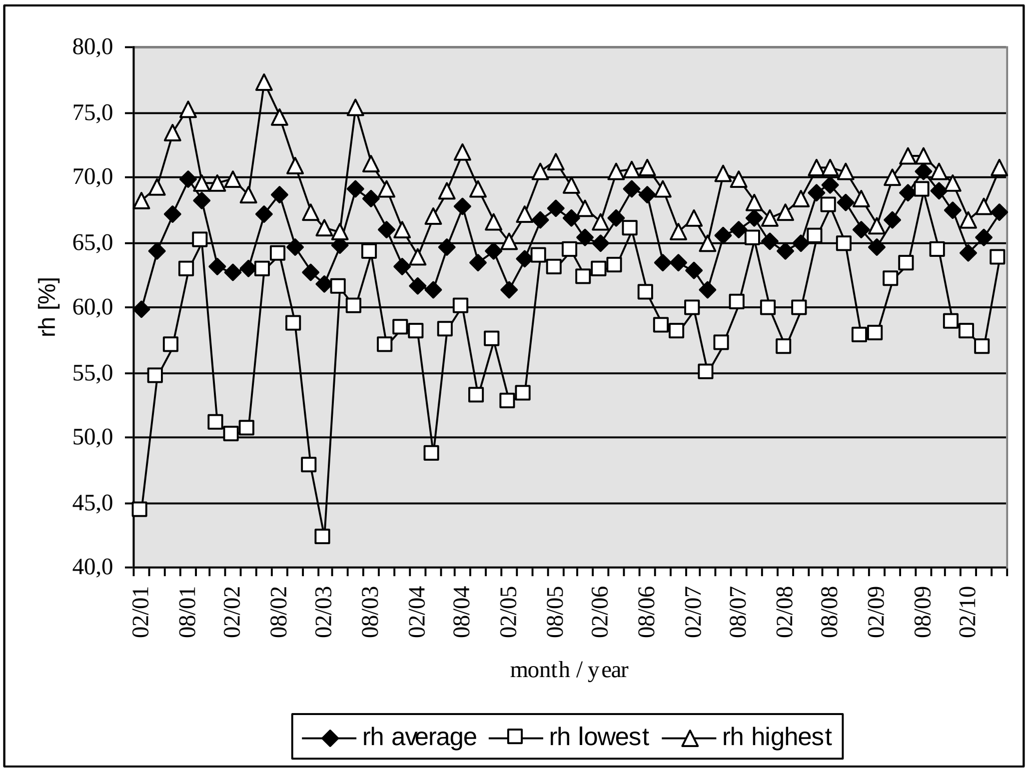

Figure 3. Development of relative humidity (rh) in the crypt from 2001 until 2010, the average monthly values are compared with the highest and lowest values respectively

Figure 3 shows the evolution of the relative humidity in the last 10 years indicating a progressive stabilization of the variations of the relative humidities in the crypt. There are two main reasons for this development:

1) The surfaces in the crypt were opened again meaning the floor has open joints now and, more important, the restoration plaster had been taken off. Thus, since 2004 surfaces with a high pore system are existing which are able to buffer the climate. At high relative humidity levels the porous building materials can absorb water molecules and at low relative humidity levels the open surfaces desorb water molecules to the air resulting in an altogether more stable climate.

2) Additionally, the intervention to the room climate leads to more stabilized levels of the relative humidity, either by controlled ventilation (if rh is too high) or by turning on the humidifiers (if rh is too low).

Applying the abovementioned measures in the crypt and monitoring the results, the damage by salt deterioration could have been reduced, but not stopped. The adjusted value of 67% of relative humidity lies in that climate area in which the salts dissolve or crystallize; therefore, little salt crystallization is to be expected.

If the adjusted relative humidity would have been exceeded the deliquescence humidity in an area with more than 75% microbiology activity will destroy the remaining wall paintings, a process which should be excluded and avoided. If, on the other hand, the adjusted relative humidity is much below the saturation humidity of the salt mixture (e.g. 60% rH) salt crystallization would be strong, as could be monitored in the winter months of January until March.

Consequently, the climate corridor, in which only less crystallization and damages take place, is around 67%. The monitoring will be continued.

7 CONCLUSION

The presented case study demonstrates the effectiveness of a constructive teamwork of Departments, architects, scientists and restorers resulting in a lasting conservation concept for an object highly contaminated by soluble salts.

In order to reduce the damages in the crypt of St. Maria im Kapitol, the combination of - on the one hand - intervention in the room climate and - on the other hand - salt extractions have proven to be effective measures. Prerequisites for reaching this result are detailed insights into the interaction between building materials, moisture, salts, and environmental conditions. The monitoring of damages in combination with salt analyses and climate measurements is a useful tool to evaluate and possibly change measures.

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