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SCIENCE and ART: A Future for Stone

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INNOVATIVE TREATMENTS AND MATERIALS FOR THE CONSERVATION OF THE STRONGLY SALT- CONTAMINATED MICHAELIS CHURCH IN ZEITZ, GERMANY

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Abstract

The sandstone of the Michaelis Church in Zeitz shows a strong decay in form of relief and alveolar weathering. The main cause for the deterioration is an extreme salt attack by magnesium sulfate. The stone as well as the weathering forms were investigated. The alveoles were desalinated by using a sprinkling method and filled by a developed hot-lime mortar. Consequently, a concept of conservation could be formulated from all the investigations and the results obtained from the treatments that could be successfully applied in a test case.

Keywords: alveolar weathering, salt, desalination, conservation

1. Introduction

The Michaelis Church in Zeitz represents a 10th century building, which has consistently undergone modifications to its façade over time. The church was constructed out of dolomite cemented sandstone that often shows alveolar weathering as a result of salt weathering (Ruedrich *et al.* 2006).

2. Preliminary investigations

2.1. Geological setting, rock material and weathering agents

2.1.1. Geological setting and rock material

The walls are constructed from the regional sandstone (Buntsandstein Formation). Hirschwald (1910) mentions quarries near Kretschau and Kuhndorf. Other large rock formations are located in the north-eastern region around the Zeitz as is shown in (Fig. 1b).

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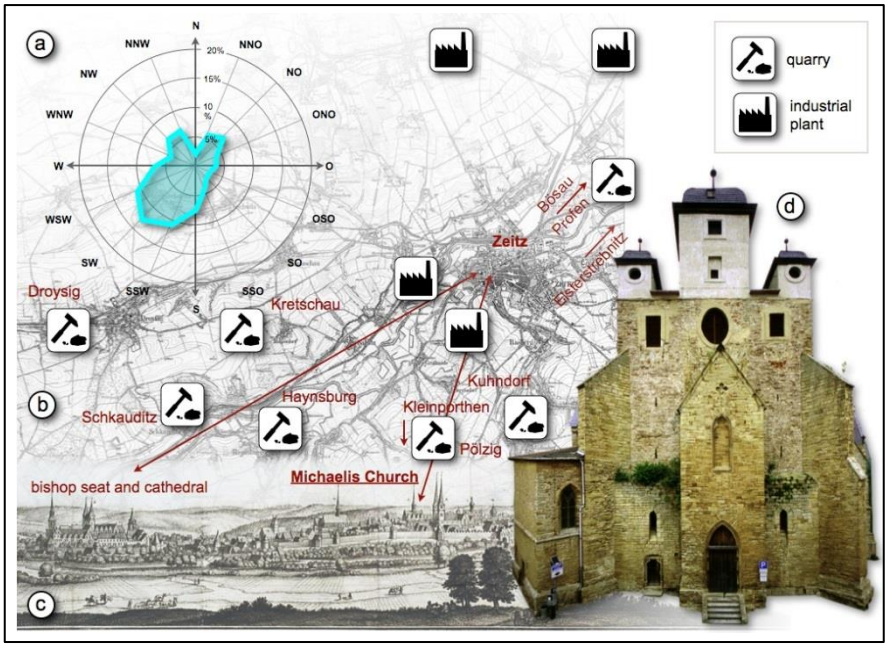

Fig. 1: a) The main wind and rain directions in percent (www.windfinder.com). b) Zeitz and its environs around 1912 with location of quarries and industrial areas. c) Lithograph of the medieval city of Zeitz from the "Topographia Germaniae" by Matthäus Merian (1593-1650), showing the outstanding historical buildings and topography. d) The western façade of the church in 2005.

2.1.2. Environmental impacts and geographical setting

During the industrial revolution Zeitz became one of the main centers for charcoal extraction and coal briquette production, starting in 1800 and continuing up into the 1990s. The briquette production factories, that produce a high content of sulfur from industrial pollution, were located near the mining areas west of the town. The church is located on a hill at the southwest of the historical city. The main wind and rain direction is from the southwest with 13.4 %, followed by a west-southwest direction with 11.6 %, and the south-southwest with 10.9 % (Fig 1a). Consequently, sulfur pollutants were transported continuously in the direction of the historical city over a period of nearly two hundred years. The impact can be seen today on the Michaelis Church, which exhibits dramatic forms of alveolar weathering on the western and southwestern side of the building (Fig. 1d, Fig. 2b).

2.1.3. Salt and weathering forms

In the case of historical buildings in Zeitz, industrial pollution in combination with the binding material of the sandstone creates a salt with a high potential for damage: magnesium sulfate. This salt results in extensive salt weathering in historical monuments as well, if dolomite-cemented stone or mortar and gypsum mortars are present (Siedel 2003, 2013, Wedekind 2014). The system of magnesium sulfate consists of three stable

crystalline phases in the atmosphere with a different number of water molecules bound within the crystalline structure: epsomite ($MgSO_4 \cdot 7H_2O$), hexahydrate ($MgSO_4 \cdot 6H_2O$) and kieserite ($MgSO_4 \cdot H_2O$). The damage potential of magnesium sulfate can be traced back to the stress generated by crystallization and hydration (Steiger *et al.* 2008). The main stress is induced by salt crystallization (Balboni *et al.* 2011). Salt weathering in Zeitz is characterized by contour scaling associated with alveolar weathering (Fig. 2).

2.2. Methods of Investigations and applied conservation

2.2.1. Petrographic and petrophysical properties of the rock

Porosity and the matrix- and bulk density were measured using hydrostatic weighting (DIN 52 102). The capillary water absorption or water uptake was measured on cubes (65 mm) with respect to the X, Y and Z directions. For the compressive strength tests, standard cylindrical specimens of 50 mm in diameter and 50 mm in length with co-planar end-faces were used and tested by a servo-hydraulic testing machine. To assess the salt weathering sensitivity of the investigated sandstone in this study, a salt-weathering test according to the standard DIN EN 12370 was performed. Polarisation and cathodoluminescence microscopy on standard thin sections were used for the petrographic analyses (e.g. mineralogical composition, grain boundary geometry, average grain size and sorting).

2.2.2. Onsite investigations

To register and evaluate the weathering damages, mappings of intensity and forms were done for selected sub-areas at the main façade of the building. Samples were taken by drill cores (Fig. 5 b). The amount of soluble salts was measured by ion chromatography and photo-spectrometry. In order to identify the crystalline salt phases, x-ray diffraction was carried out.

2.2.3. Desalination and evaluation

Salt reduction is a basic prerequisite for a sustainable restoration. The most suitable desalination method is dependent on a number of factors. Factors that need to be taken into account are the rock material, the degree of contamination and depth and type of salt responsible for the damage. It becomes clear that the contamination detected at depth can not be reached by the poultice method (Fig. 4b) and the drying rate of the material is quite small. In general, immobilization of the salt by chemical ionic exchange and subsequent precipitation would be possible but in this case difficult to control. For this reason the sprinkling method was chosen as the most effective technique in terms of function, time and costs. To evaluate a suitable conservation treatment a strongly weathered pillar was chosen as a test case. The surface of the pillar was divided into different treatment sections (Fig. 2). The development of weathering was documented by using historical photos (Fig. 2a to 2c).

The sprinkling method was developed for the desalination of salt contaminated tafoni of the rock cut façade in Petra/Jordan (Wedekind, Rüdrich 2006). The method was already used successfully for the desalination of architectural elements at the Franciscan Church in Zeitz (Wedekind, Rieffel 2014). Through spray nozzles, connected within a raster-like pipe system, water was sprayed on the different sections. The water running down the pillar was collected and measured by electrical conductivity. At the beginning of the procedure the water is predominantly absorbed by the porous stone surface through capillary forces. Water absorption is dependent upon the transport properties of the material. These are

controlled by the pore space properties, such as porosity and pore radii distribution, and are a time-dependent process (Wittmann 1996).

At the lower end of the treated area a drain gutter was constructed from clay, so that the eluate can be funneled into a sample container. Excess water not absorbed by the stone was collected in five liter amounts and measured for electrical conductivity (mS/cm). Fifty liters of eluate were collected and tested in five liter amounts per cycle. The sprinkling was terminated after a treatment of about 10 minutes. After every sprinkling cycle, a break of one week was observed in order to initiate the drying procedure, which leads to the concentration of salts in the near-surface area of the stone.

Five cycles were done over a period of three months. The correlation between the electrical conductivity and the real content of soluble substances within the eluate was calculated by evaporation of different samples consisting of one liter eluate in a drying oven and weighing. Consolidation was not necessary because all the unstable material was removed by the smooth washing process of desalination.

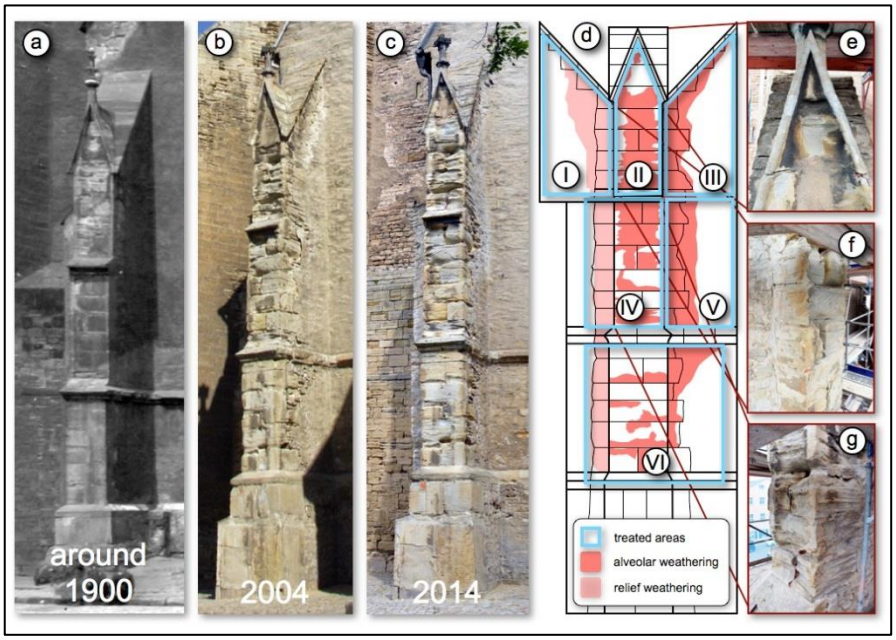

Fig. 2: a-c) The chosen pillar during different years. d) Architectural drawing with weathering conditions and treatment areas and e-g) alveolar weathering forms in detail.

2.2.4. Material physics of the restoration mortar

As a finishing mortar for restoration a modified hot-lime mortar was configured. To reduce and to control the speed of thermal reaction as well as to enhance the workability, an additive of a hydraulic binder was added to the dry mortar mix. The change in reaction could by measured by thermal expansion and temperature. Crushed and sieved sand made from the local sandstone with a grain size distribution ranging 0.1-0.5 mm was used as

aggregate to create compatibility with the stone material. Specimens after DIN EN 196-1 (4×4×16 cm) of different mortar mixes were made: The binder/aggregate composition of the hot lime mortar was 1:3. Main binding material of the specimens for the hot lime mortar was unhydrated lime Cl 80 Q modified with white Portland cement (WC) in different ratios. During the process of hardening, the surface temperature as well as the dilatation was measured on the specimen top to evaluate the intensity of the exothermic reaction and the process of expansion and shrinking. After 28 days of drying under the same conditions, porosity, density and flexural (FS) and uniaxial compressive strength (UCS) were measured.

3. Results

3.1. The sandstone

3.1.1. Petrography

The sandstone of Zeitz mostly has a yellow color. Besides these varieties, which clearly dominate the stone architecture of the town, grayish to greenish types are also present. The medium sandstones show a good parallel or obliquely layered structure. Many sedimentary structures like cross bedding and wavy lamination, mudcracks and ripple marks are observable. The sandstones show grain sizes ranging 0.2 to 0.5 mm, are poorly rounded to angular, well-sorted grains of polycrystalline and monocrystalline quartz (50 - 60% vol.), feldspars (35 - 40%) and lithoclasts (<10%) and are embedded in dolomitic cement. The rather coarse cement proportion (40%) is dolomitic and shows a clearly oolithic texture (Fig. 3 a), causing a very strong reduction in porosity. The secondary porosity is caused by a local, minor dissolution of the cement and its values range 1 - 3% of the whole rock (very poor porosity) (López-Doncel et al, 2002).

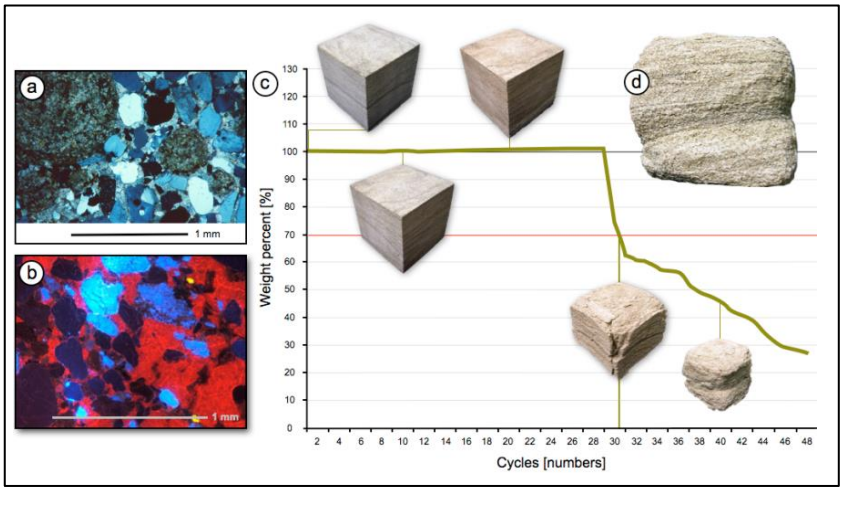

Fig. 3: a) Thin section of the Zeitz sandstone Rounded oolithes are visible in grains of mono- and polycrystalline quartz) and feldspars, which are embedded in a dolomitic matrix. b) Thin section under cathodoluminescence. c) Salt bursting test and d) weathering related to the bedding.

The color of the stone is due to high concentrations of feldspar, mica and clayish substances clearly identified by CL-microscopy (Fig. 3b). The dolomite cement could be determined by cathodoluminescence microscopy (red), clay is blue and feldspar shows a light blue color (Fig. 3b).

3.1.2. Petrophysics

The rock material has a low porosity that varies between 3 and 15 % with a dominance of macropores, and contains a homogeneous fine to medium grain size with a clearly visible layered structure. The dolomite cementation varies between 13 and 76 % by volume, and therefore reaches a density of 2.72 g/cm^3. The stone has a low water uptake rate (averaged 0.8 kg/m^2 that varies as much as 46 % with the bedding direction. Compressive strength with 100 N/cm^2 is quite high as compared to other sandstones. This may be the reason why the stone shows a good resistance to salt bursting, which was performed on cubic samples 6.5 by 6.5 cm in size and submersed in a 10 % $NaSO_4$ solution (DIN EN 12370). A material loss of 30 % after 30 cycles could be determined (Fig. 3c). After discoloration due to iron oxidation, a massive contour scaling starts at the 20th cycle and continues with further material loss (Fig. 3c). In the last stage a weathering related to the bedding is observable, which can also be found at the church building (Fig. 3d).

3.2. Weathering forms and agents

3.2.1. Weathering forms

The sandstone blocks show severe deterioration with weathering depths up to 30 cm (Fig. 4a to Fig. 4c). The main decay phenomena are two different types of weathering, relief and alveolar (Fig. 4a). Dark crusts and discolorations are of only subordinate importance. Weathering is characterized by heterogeneous back-weathering, which depends on the bedding of the sandstone. The relief "weathering type I" represents a modified alveolar weathering, which is characterized by deep gouges. The material loss is dominated by granular disintegration. For "relief weathering type II" the weathering intensity is slight with up to 3 cm. Strong back-weathering also follows the bedding of the sandstone. This weathering form achieves back-weathering rates up to 30 cm. The material loss in the gouges is dominated by flaking and contour scaling. Relief weathering type II is located at areas of direct water action, whereas relief weathering type I and strong back-weathering occurs in expositions protected by water run-off but effected by moisture penetration.

3.2.2. Salt-weathering

The x-ray diffraction shows that different magnesium sulphate hydrate phases are detectable. Next to epsomite ($MgSO \cdot 7H_2O$) and hexahydrate ($MgSO \cdot 6H_2O$) kieserite ($MgSO \cdot H_2O$) also occurs (Fig. 5a). The quantitative salt analyses show that the salt content of magnesium sulphate from samples of relief type II is much higher than those of relief type I (Fig. 5b). Some samples taken out of the alveolar weathered areas show a contamination that reaches a profile depth of more than 10 cm (Fig. 4b and Fig. 5).

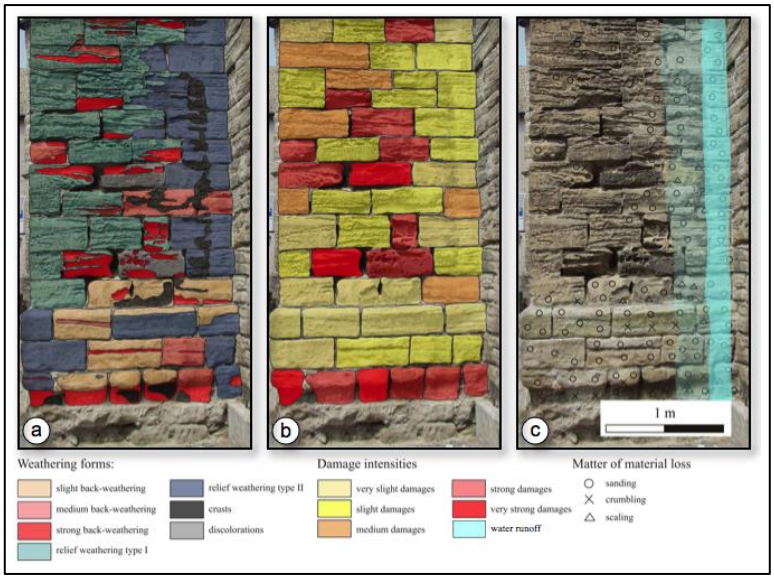

Fig. 4: a) Weathering forms, b) damage intensity and c) reasons for material loss at the testing area.

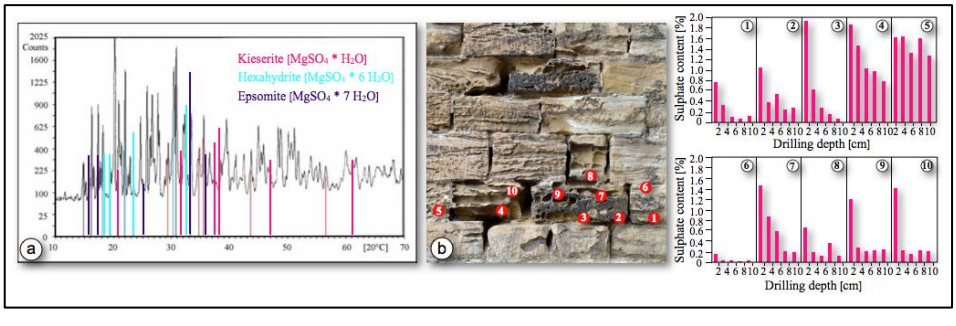

Fig. 5: a) X-ray diffraction of the salt efflorescences shows different MgSO-phases. b) Quantitative salt analyses in the depth profile taken from different weathering zones.

3.3. Conservation/restoration

3.3.1. Desalination

Around 1100 g of soluble material could be extracted, while the desalination rate of the different sections differs between 21 g/m^2 and 71 g/m^2 according to the intensity of weathering (Tab. 1). The effect of desalination was also tested by drill dust samples that show a significant decrease of salt load after treatment.

Tab. 1: Summary of results from the desalination.

Sprinkling area	Sum of electrical conductivity	Total salt content	Rate of desalination
	[mS/cm]	[g]	[g/m^2]
I	61.68	88	22
II	121.32	173.3	69.3
III	187.66	286	67
IV	86.91	124	31
V	201.46	288	71
VI	97.76	140	21
Total / ∅	757.78	1099	44 ∅

3.3.2. Restoration

During the hardening of the pure hot lime mortar (Cl 80 Q), the temperature rose from 21°C to 45.7°C in a period of 10 minutes (Fig. 6a). The expansion reached 0.8 mm, a percentage of 2 % and exhibits a low shrinking tendency (Fig. 5b). The specimens modified with the white cement (WC) attained temperatures of 29.6°C/8min to 37.3°C/18min (Fig. 7a). No shrinking took place but a moderate expansion ranged between 0.1 mm and 0.5 mm (Fig. 6b). The mortars modified with white cement reach up to two times higher values of compressive strength (USC) and flexural strength (FS) than the pure hot lime mortar (Fig. 6c). The different amounts of the hydraulic additive result in an increase from 1.42 MPa to 2.05 MPa in the case of USC and from 0.58 MPa to 0.98 MPa for FC as shown in Fig. 6c.

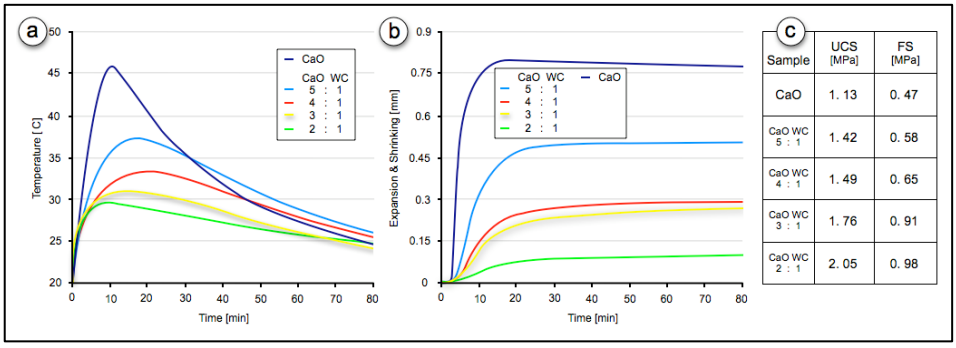

Fig. 6: a) Exothermic reaction of the different mortar mixes and b) expansion/shrinking of the different mortar mixes. c) Compressive and flexural strength of the different mortars.

4. Final Conclusions

The results of these investigations lead to an understanding of the weathering process and the development of a suitable conservation strategy. By using the described sprinkling technique for desalination, a control of the process was immediately possible by electric conductivity measurements. This allows a calculation of the contamination as well as the planning and application of the whole desalination process. The hot lime mortars show interesting properties for stone conservation and restoration. According to the results, a fractional amount of white-cement improves the mechanical properties as well as the workability of the material. For restoration the variety with a CaO:WC ratio of 3:1 was chosen. Structural interventions can be prevented in the historical building by the desalination and mortar filling method, thus costs can be reduced by around 30%. Furthermore, by conservation instead of traditional restoration the church can be restored close to the international regulations of conservation as defined in the "Charta of Venice" and other regulations of ICOMOS (International Council on Monuments and Sites).

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