

Analysis of the Salt Content during Water Bath Desalination of a Polychrome Limestone Relief

Sebastiaan Godts and Camille De Clercq
Royal Institute for Cultural Heritage (KIK-IRPA)
Jubelpark 1, 1000 Brussels
e-mail: sebastiaan.godts@kikirpa.be

Abstract

In 2009 a polychrome limestone relief from the 15th Century was discovered in the masonry of an altar in the town of Merbes-le-Château. Due to rising damp a high amount of salts accumulated in the first centimeter of the sculpted surface, containing a salt mixture of 2 w% nitrate salts, sodium chloride and up to almost 7 w% of calcium sulfate. It was considered necessary to remove the relief from the masonry and carry out a desalination treatment by immersion in water. Throughout the water bath desalination the polychrome surface was protected with cyclododecane. The ion content of the water was measured regularly, by ion chromatography. After 3 baths, 260 immersion days in a tank containing approximately 140 l demineralized water, a slow drying procedure was carried out. Both protection of the polychromy and desalination proved effective.

Keywords: Salts, Water Bath, Desalination, Polychromy, Avenderstone, Cyclododecane, Ion Chromatography

Introduction

In 2009 a polychrome limestone (Avenderstone) relief (84x64x14 cm) was discovered in the masonry of an altar from the church of Saint-Martin in the town of Merbes-le-Château (Belgium). The commemorative relief is dated 1443 and represents Jehan Jamet, his family, Saint John the Baptist and the Virgin with child (Bedoret 2010). It was hidden, presumably as a protective measure, behind the antependium of an altar (Figure 1).



Figure 1: The relief as it was discovered in the church.

The relief was exposed to constant rising damp and fluctuating climatic conditions, causing salts to accumulate and cause damage at the drying front near the sculpted surface. After preliminary investigations it was considered necessary to remove the memorial from the masonry and carry out a desalination treatment by immersion in water. However, remains of water soluble polychromy on the surface needed to be protected with a coat of cyclododecane (CCD), applied as a melt. The specific conservation procedures and materials are described in De Clecq & Godts (2020). The ion content in the stone and the bath water was analyzed by ion chromatography before, during and after the bath desalination. Together with the salt analysis, the physical characteristics of the stone were determined to support the conservation treatments.

Experimental

The Avenderstone (*Pierre d'Avesnes-le-Sec*) is found in the north of France and is a fine-grained white limestone with clusters of glauconite (Dusar, et al 2009). The physical characteristics of the Avenderstone were taken from Godts, et al. (2015). The capillary water absorption and the drying behavior of the Avenderstone are determined on 6 block samples with different dimensions. Capillary water absorption was carried out according to the guidelines of RILEM-UNESCO 1978, n° II.6, average results are presented. The capillary water absorption

coefficient is derived from the slope of at least 5 successive points of the first linear part of the curve (water absorption expressed as g per m² as a function of time (s^{0.5})). After the capillary water absorption test, the samples are immersed in demineralized water for 48 hours, from which the water-borne porosity is derived, before performing the drying test. In order to determine the drying behavior of the samples they were covered with tape on all sides so that only the test surface is open. The samples are weighed every hour for the first 8 hours and twice a day from the second to the fifth day. Climatic conditions during execution were 23°C and 50-55% RH. The total porosity and densities are determined from 3 samples of the stone by mercury intrusion porosimetry (MIP) (Micromeritics Autopore IV). For the purpose of this paper a select amount of data is shown.

The ions and quantitative distribution within the stone of the relief of Merbes-le-Château are determined by analysis of powder samples (Ø 6 mm), drilled to a depth of 6 cm. The samples are taking in intermediate steps from each centimeter to achieve an in-depth salt profile. Samples are taken from two locations (zone I and zone II) (Figure 2), 12 samples before treatment and 12 after. The ions (anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺)) are quantified by ion chromatography (IC, Metrohm). From the excess of cations the amount of soluble carbonate (CO₃²⁻) was calculated.



Figure 2: The location of the samples before desalination (left: zone I and right: zone II). Samples after desalination are taken just above the initial samples (not shown). The (testo) probe that was placed in the drill hole shown left (zone I) logged the RH en T during the drying process.

The results in parts per million (ppm) are converted into mol/g and presented in this paper as w%, more specifically, weight percent in comparison to the weight of the stone sample. The ions in the water bath (as described further) are, however, represented as milliequivalents mEq(/g) to represent the balance between anions and cations graphically (raw data is available on request). The salts detected in the stone were investigated with the ECOS/RUNSALT model (Price 2000) (Bionda 2006) to understand the salt mixture and its behavior in changing climatic conditions. The data is entered into the RUNSALT software as mol, following the procedure described in Godts, et al. (2017). Efflorescence was identified with micro-Raman spectroscopy (Renishaw InVia). The measurements were carried out with a 780nm near infrared diode laser through a long-distance objective with a magnification of x5 or x50 reaching approximately 17,7 mW or 14,3 mW at the sample. An exposure time of 10 sec and a measurement range between 100.00 and 2000.00 cm^{-1} was sufficient to obtain identifiable spectra.

After initial conservation treatments and protection of the polychromy with a melt of cyclododecane (see De Clercq and Godts (2020)) the water bath desalination procedure was carried out as followed: Slow capillary absorption with demineralized water from the base of the object (84x14 cm) in vertical position, after 11 days the object is placed horizontally (84x64 cm) with the sculpted and protected surface upwards and the tank (water-bath) is filled with approximately 140 l demineralized water (Figure 3).

To accelerate the diffusion of ions into the water, a pump is placed in the tank to create a constant flow around the object. A total of 3 baths (replacing the water twice) was carried out. The time and water content are respectively per bath: 112, 119 and 29 days; 139.27, 142.52 and 140.00 liter. During a total of 260 days 156 samples are taken from the bath by mixing the water and removing 10 or 20 ml of water to determine the ion content as described before. Each time water is removed the total water content in the bath is

recorded. After desalination the water is removed from the tank and the object is left to dry slowly over 99 days. During drying the object is left in the tank, closing the box over 24h when the RH lowered below $\pm 75\%$. Thus, the relative humidity (RH, %) and temperature (T, °C) are recorded (every 5 min.) in the tank, in the immediate vicinity of the object (onset, HOBO, temp/RH logger). In addition, the RH and T in the depth of stone is recorded with a probe placed in the drill hole made for sampling and salt analysis. The probe is placed in the stone at a depth between 1.5 and 5 cm (Testo thin moisture and temperature sensor with a length of 3.5 cm; and recorded with Testo 635-2).



Figure 3: The object is placed horizontally with the sculpted and coated (cyclododecane) surface upwards in a tank filled with ≈ 140 l demineralized water.

Results and Discussion

The average results of the measurements on the Avenderstone aided the understanding of the water uptake, drying and the determination of the salt distribution during the desalination processes. The stone has a high content of capillary active fine pores with an absorption capacity (Acap) of $0.34 \text{ kg/m}^2 \pm 0.5$ (0.01 (StDev.)). A total available water capacity (Wcap) of 330.9 kg/m^3 (20.5 (StDev.)) and a density (ρ) of 1.56 kg/dm^3 (0.05 (StDev.)). The first drying phase of the Avenderstone is characterized by a rapid linear weight reduction that takes about 190 hours (≈ 8 days) (on average). The moisture content at this point is called the critical moisture content and amounts to about 40% of the saturation moisture

content. After 680 h (≈ 28 days), approximately 9% of the original moisture content remains. Derived from the MIP measurements the bulk density at 0.51 psia was verified to be 1.573 g/mL (1.57 kg/dm³), an apparent (skeletal) density of 2.668 g/mL (2.67 kg/m³) and a porosity of 41.0%.

The salt mixture was investigated with the Runsalt model (Figure 4). The mixture mainly contains nitrates that can be linked to, calcium, potassium, magnesium and sodium. The remaining salts can be identified as chlorides linked to sodium, potassium and magnesium. The latter two possibly forming a small amount of the hydrated double salt carnallite, below 30% RH. Crystallization can however start at drying conditions below 50% RH, beginning with sodium nitrate followed by sodium chloride. Below 35% calcium nitrate can crystallize, followed by magnesium- and potassium nitrate. To prevent crystallization while the relief remained in the workshop (before desalination), it was placed in a closed box with a saturated solution of sodium chloride, maintaining a RH of $\approx 75\%$, all salts, excluding gypsum, remained in solution.

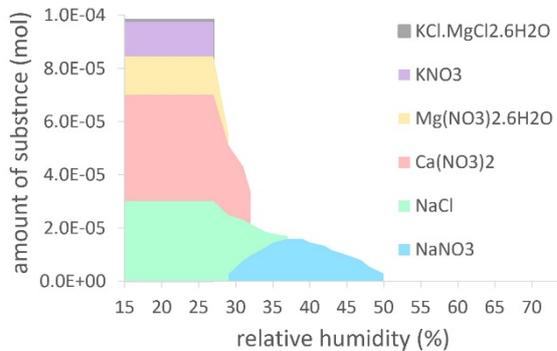


Figure 4: Runsalt output of the ion content detected in the first centimeter of zone I (excluding equimolar contents of calcium and sulfate ions, and excess of calcium), revealing the crystallization behavior at 20°C in changing RH (%).

Before and after the treatment the salt content in the depth of the stone was analyzed considering the total ion content excluding equimolar amounts of Ca+SO₄ (considered as the gypsum content). From the results it can be derived that the total salt content in the stone (avg. 0 to 6 cm, zone I and II) decreased from 1.6 w% before

desalination to 0.2 w% after desalination (Figure 5). Separately represented is the content of CaSO₄ before and after treatment, a similar decrease was shown for the gypsum content from respectively 1.2 to 0.3 w% (Figure 6).

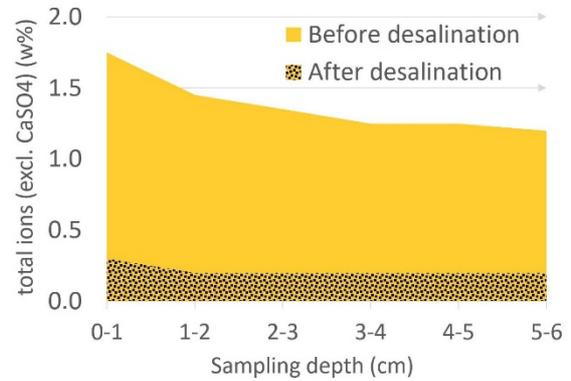


Figure 5: Graphical representation of ion content (w%) per centimeter depth (avg. of zone I and II), excluding equimolar amounts of calcium and sulfate. On the X-axis from left to right the sampling depth in the stone starting in the sculpted surface. The full stacked area represents the salt content before desalination and the dotted stacked area after desalination.

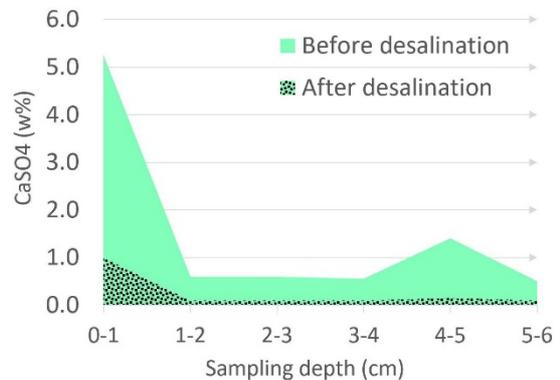


Figure 6: Graphical representation of the CaSO₄ content (w%) (avg. of zone I and II). The full stacked area represents the gypsum content before desalination and the dotted stacked area after desalination.

The ion content of the bath water was regularly measured by ion chromatography to determine when refreshing the water was required. When the ion concentration in the bath slowed down the bath water was replaced. The salt content diffused into the water reached a total of 728 grams over

260 days (Figure 7). Although the ion concentrations slowly continued increasing during the last bath, it was cut short as the salt concentration was theoretically considered sufficiently low in the object. As described earlier this was later proven in the analysis of the salt content in the stone before and after desalination.

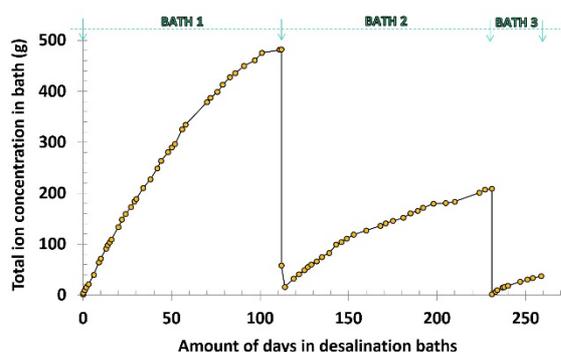


Figure 7: The salt content (gram) detected in the bath water over time (days). The salt content diffused into the baths reached a total of 728 grams over 260 days. 156 samples were analyzed. The specific time and water content are respectively per bath: 112, 119 and 29 days; 139.27, 142.52 and 140.00 liter.

During the desalination procedure the investigations into the equilibrium between anions and cations allowed the identification of the diffusion processes of ions into the water over time (Figure 8).



Figure 8: Graphical representation of the anions and cations (mEq) detected at the end of each desalination bath, the ion content logically builds up over time as shown in figure 7.

The imbalance between anions and cations remains on average 0.0780 mEq/g with a standard deviation of 0.1016 mEq/g on 156 samples. A high amount of nitrate and calcium ions are detected, followed by chloride, magnesium and sodium ions and smaller amount of potassium and sulfate ions. The equilibrium between nitrate and calcium ions

is almost balanced in the second bath, while the content of calcium and sulfate increases over time. This trend can be explained by the slower dissolution of the lesser soluble salts that are present at higher concentrations near the temporary hydrophobic coating (CCD) at the sculpted surface. The results of the ions detected in the baths correlate with the analysis of the ions detected in the stone.

A white crust was seen on top of the polychromed stone surface and identified as gypsum by micro-Raman spectroscopy (not shown). The crust became clearly visible after desalination and the final removal of the crust proved to increase the visibility of the sculpted forms significantly when compared to the relief when it was discovered (Figure 9).



Figure 9: Detail of the relief before and after desalination. Left: before treatment; Middle: gypsum on the surface after desalination and the sublimation of the CDD; Right: after removal of the gypsum crust.

Conclusions

The analysis of the salt content in the stone explained the deterioration of the sculpted surface when it was discovered in the church, thus the removal of the relief from the masonry was deemed necessary. While investigations into the desalination procedure and protection of the polychromy were under way, the relief remained in a stable environment above 75% RH, which was established with a saturated solution of sodium chloride. This humidity was considered on the basis of the detected salts and theoretical approach with the Runsalt model. However, seen salt mixtures are widely understudied and the model doesn't consider salt kinetics a higher relative humidity was chosen to make sure all salts (excluding gypsum) remained in solution.

After initial conservation and protection of the polychromy the water bath desalination was started. The procedure was specified on the basis of the stones physical characteristics and allowed the understanding of water uptake, ion diffusion into the water bath and the drying behavior. However, seen the theoretical approach it remained important to follow the ion content in the water bath and the drying of the stone during the process. Following the ion content in the bath aided the understanding when diffusion slowed down to define the optimal time when water needed to be renewed. The drying of the stone was followed by keeping the object in higher RH, which allowed a slow and controlled drying process.

The results show that cyclododecane as a melt offers considerable protection for water-sensitive polychromy on limestone during a long term water bath desalination. Diffusion of ions into the water bath was slow as the salts at the surface under the hydrophobic coating needed to dissolve and migrate up to 14 cm through the porous structure of the limestone into the water bath. Due to the long term immersion it was important to continue IC measurements to identify the specific ions that were diffusing into the bath. With each measurement the equilibrium between anions and cations was checked to identify an access of calcium, which would indicate the presence of dissolved calcium carbonate. Seen that the equilibrium remained relatively stable throughout the process it was deemed safe to continue the desalination.

The long term immersion in a high quantity of water also allowed more gypsum to dissolve and diffuse into the bath. After 3 baths over a period of 260 days and 99 days of drying the analysis of the salt content in the stone showed an 88% reduction of the salt content (excluding gypsum) and a 75% reduction of the gypsum content (on average) from 0 to 6 cm starting from the stone surface. In the meanwhile the object has been returned to the church and stands on a stone pedestal without any specific needs for conditioning as the salt content is considered sufficiently low.

References

- Bedoret M. 2010. Invisibles depuis 200 ans? le trèfle n°69, 15.
- Bionda D. 2006. Modelling indoor climate and salt behaviour in historical buildings: A case study, PhD thesis, Diss. Nr. 16567 ETH Zürich.
- Bromblet PH., Vergès-Belmin V., Franzen C., Aze S., Rolland O. 2011. Toward an optimization of the specifications for water bath desalination of stone objects. In: I. Ioannou & M. Theodoridou (ed.): Salt Weathering on Buildings and Stone Sculptures. Cyprus: 397-404.
- De Clercq, C. and Godts, S. 2020 (in print). Cyclododecane as protection for water-sensitive polychromy during water bath desalination of lime stone sculpture: a case study of a mid-fifteenth century wall-mounted memorial from the Burgundian Netherlands. Proceedings of ICOM-CC 19th Triennial Conference, Beijing, China, 14–18 September 2020.
- Dusar M., dreesen R., De Naeyer A. 2009 Nattuursteen in Vlaanderen, versteend verleden. Kluwer, Mechelen, 135-146
- Godts S., Fontaine L., Debailleux L., Hayen R., De Clercq H. 2015 (internal report). Proefbehandeling zoutextracties, klimaatstudie en mortelanalyse, Gent OLV St.-Pieterskerk. KIK-IRPA report, Brussels D.I: 2013.11990
- Godts S., Hayen R., and De Clercq H. 2017. Investigating salt decay of stone materials related to the environment, a case study in the St. James church in Liège, Belgium. Studies in Conservation, vol. 62, no. 6, 329-342
- Price C. (ed.). 2000. An expert chemical model for determining the environmental conditions needed to prevent salt damage in porous materials. European Commission Research Report No 11, (Protection and Conservation of European Cultural Heritage). London: Archetype Publications.