WATER BATH DESALINATION OF SANDSTONE OBJECTS

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Abstract

Water bath desalination is a widely used technique in restoration. To understand the behavior of the salts, their distribution during the measure and their movements a case study was analytically documented. The example of a sandstone vase from the Dresden Zwinger showed interesting results. The salt solution in the water bath concentrates on the bottom of the water trough. The composition in the desalination water changes over time. Salts are redistributed in the desalinated object by the final drying. The drying at the end of the measure is proceeded as very effective poultice desalination. Water bath desalination can be monitored and maintained by regular measurement of the electrical conductivity of the bath water.

Keywords: restoration, salts, desalination, conductivity, poultice

1. Introduction

Soluble salts are identified as the major driving forces in deterioration of sculptural and monumental stone. Most damage features and great loss of damage of building stone is due to salt induced deterioration. Thus the desalination of the material has become a crucial step in restoration. Desalination, in terms of this paper, means the reduction of the salt content in a porous system. Various desalination techniques are frequently applied to cultural objects. Vergès-Belmin and Siedel (2005) reviewed the desalination of masonries and monumental sculptures by poulticing. Here we focus on the other major desalination technique for stone: the water bath desalination.

The treatment of desalination in natural stone restoration has its first documented roots in the beginning of the 20th century. Rathgen (1915) reports about chemical monitoring of the desalination of Egyptian objects of art in water bath in 1890. Thus the water bath desalination technique can be regarded as the earliest measure within this field. Furthermore already Rathgen (1915) demonstrates how scientific attendance may control and improve the practical action. In following decades the attention to desalination is less intensive and barely documented. However, in the last few years scientific approach to salt related weathering has seen a great revival, only the statements for practical action as consequence to the extended knowledge to restore the cultural heritage are rare.

To date water bath desalination is mostly performed on small objects mainly from archaeological origin (e.g. Koob & Won Yee 2000, Pessoa et al. 1996). In our case study we present the water bath desalination as a routine desalination measure on sculptural sandstone objects. Several restoration measures were analytically accompanied to receive a better insight in the processes during desalination. Poultice desalination is slightly touched in this paper as final drying of the objects is executed with the use of a poultice.

2. Materials and methods

2.1 Sandstone objects

The water bath method presented here has been performed as a routine procedure in the restoration workshop of the Dresden Zwinger (built 1711-1728) since the 1990ies. The façades of the baroque building contain more than 680 vases and figures. They are carved of local Cretaceous sandstone from the Elbe valley. It is mature quartz sandstone with more than 90 % quartz content in most cases. The so-called "Cotta type" sandstone preferentially used for sculptures contains some clay mineral content (illite, kaolinite) but no soluble minerals and has a total porosity of about 20 vol-%.

The inner city of Dresden was highly polluted by coal combustion in the 20th century, resulting in encrustation and formation of soluble salts on most historical sandstone objects. Sulfates are the dominating salts also found on the Zwinger sculptures (Siedel & Klemm 2000). They obviously force stone deterioration and have to be removed in the course of conservation. The sandstone sculptures are moveable and their surfaces are normally stable enough to survive water bath desalination without relevant loss of material.

2.2 Desalination steps

The routine measure of water bath desalination in the workshop of Dresden Zwinger can be divided in three steps: pre-wetting actions, water bath and post measures. The first step of restoration before applying a water bath to a stone sculpture is the cleaning of the total surface. Experiences show that often a great deal of the salts sits in the dust on the outer side to the surface. Tests comparing the amount of salts moved by desalination from an uncleaned to a cleaned sculpture have shown clear results (Hoferick 2005). The removal of these potentials can be performed with adjusted brushes or blasting. Water tanks were built for the objects. Wooden constructions were disrobed with waterproof foil big and strong enough to host the object and several hundered litres of water (fig. 1). The troughs were covered to avoid dust entry. Deionised water from a Reserve Osmose RO3 apparatus (Werner Company) was used to totally immerse the objects. In routine procedure, the whole water is changed in cycles after several days or weeks following the results of daily measurements as will be discussed below. In the case study presented here in more detail (vase O12), the procedure was slightly modified by taking a part of the water bath off from the bottom of the tank and adding the same volume deionised water at the top. The third step of desalination is the drying of the object combined to a poultice procedure, i.e. the application of a wet cellulose poultice to the drying surface to avoid efflorescence on the stone. After all further conservation procedures like consolidation, anchorages and surface treatments follow.

2.3 Analytical monitoring

The extraction of salts from the sculptures in routine procedure is monitored by daily measurements of the electrical conductivity in the water troughs. In case of object O-12, anions and cations were additionally analysed by ion chromatography in selected water samples.



Figure 1. Sandstone vase in water bath for desalination in routine procedure.



Figure 2. Correlation of conductivity to laboratory determined dry residue data of the samples from workshop water bath desalination measures.

Electrical conductivity and total dissolved solids

Salts dissociate in water. The ions determine the conductivity properties of the solution. The electrical conductivity is given in Siemens per meter (S/m) or µS/cm, respectively. The electrical conductivity is reciprocal correlated to the electrical resistance which is determined. The daily measurements of electrical conductivity in routine procedure are carried out by a transportable, outdoor suitable instrument (HANNA HI 991300) after stirring the whole water bath with a rotary pump for 15 minutes to get a homogeneous ion distribution. The conductivity is a criterion for the amount of salts soluted. The solid content of a solution can be displayed as the dry residue, indicated in milligrams per liter, that is obtained in the laboratory by evaporating the water and gravimetric determinating the remaining. Hölting (1996) shows that the dry residue of a solution can be approximated by the multiplication of the electrical conductivity with a factor m = 0.725. Here we use TDS (total dissolved solids) values as the calculated solids on the basis of the measured conductivity. Own tests with the salt mixtures extractable from Zwinger sculptures have shown that the TDS-calculation is an appropriate procedure to achieve results comparable to the dry residue (fig. 2).

Ion chromatography

Quantitative salt analyses were carried out by the ion exchange chromatography system Dionex IC90. In order to understand and differentiate the diffusion processes of salt ions from the sculptures into the trough during water bath desalination the salt ions $SO_4^{2^-}$, NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} were analysed in selected water samples.

3. Results and discussion

In the course of the case study the object O-12 was set in a normal upright position in the bath on a 40 cm pedestal (fig. 3). This is a modification in set up compared to the routine procedure. But salt solutions have a higher density than pure water, i.e. the salt concentration in a water bath is expected to be higher at the bottom than at the top level. The gradient between salt concentration in the sculpture and in bath water is the driving force for the desalination process following the principle of ion diffusion. From this point of view it should be useful to specifically remove high-concentrated solution from the bath. Thus, a methodical approach modified from the routine treatment was made to vase O-12. 60 liters of salt-containing water (ca. 7 % of total bath water) were daily pumped out from the bottom of the trough and 60 liters of fresh, deionised water were added on the top of the trough afterwards. Conductivity was measured every day just before water exchange at 17 different height levels (average of 4 measurements each) in the trough. In fig. 3 the water depth profile of conductivity is given for the 7th day. The bars are given as conductivity and is resulting TDS on the upper x-axis.



Figure 3. Vase O-12 on pedestal and conductivity profile in bath water on 7th day.

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After 29 days the daily water exchange was stopped and after 56 days the vase was removed from the trough. Fig. 4 shows the development of conductivity at five selected levels over the whole time of bath desalination. Over the first 7 days, there was a permanent increase in salt content at the bottom level even if the water was daily removed from this position. In the following days salt content was permanently decreasing, i.e. more salt is removed with the pumped-out water than can be migrating to the water again within the next day. The same effect is displayed in fig. 5 with regard to the salt removed with pumped-out water every day. After stopping the daily water exchange at day 29, salt conductivity in the water bath without exchange was increasing again, but at a significantly lower level. Furthermore, differences between measurements at different height levels are low.



Figure 4. Conductivity measurements at selected depth levels (cm) in the water bath during desalination of vase O-12. "0 cm" is at the top, "160 cm" at the very bottom of the trough.



Figure 5. Daily removed salt quantity pumped out with water at the bottom of the trough during the first period (28 days) of desalination of vase O-12.



Figure 6. Daily removed salt ions from the bottom of the basin with in first period.

Fig. 6 does show the development of anion concentration within the removed water of the first desalination period. Parallel to the quantity of total salts (fig. 5) the sulfates show a very similar evolvement. To a lower degree nitrates follow this but chlorides stay on a flat concentration. In tab. 1 the IC-analysis of five water samples of the first period and one final sample before bath end are given.

day	СГ	NO ₃	SO4	Na^+	K ⁺	Ca ⁺⁺	Mg ⁺⁺	NH_4^+	total	balance
1	0.06	0.14	1.96	0.07	0.08	1.38	0.23	0.30	4.22	-0.09
7	0.07	0.20	2.95	0.08	0.08	2.09	0.37	0.45	6.28	-0.16
14	0.07	0.23	1.73	0.08	0.06	1.33	0.20	0.10	3.82	-0.26
20	0.07	0.15	1.03	0.09	0.04	1.05	0.12	0.00	2.56	0.06
28	0.06	0.04	0.67	0.10	0.04	0.53	0.08	0.00	1.52	-0.03
56	0.15	0.19	1.26	0.15	0.07	0.95	0.16	0.08	3.01	-0.19

Table 1. IC-Analyses of selected water samples from the bottom of the basin (O12) with ion-balances (cations minus anions), all data in equivalent concentration [mEq/l]



Figure 7. Distribution of total salt contents from drill powder profiles on vase O-12 before desalination, after water bath and after poultice treatment.

The last step was the drying process. A wet cellulose poultice was applied to the whole surface of the vase immediately after removing it from the bath. The workshop atmosphere was 17 to 26 °C and around 45 % r. h. during the drying process. Water evaporates at the interface water to air. This interface is on the outer surface to the beginning but successively moves inside. In the zone of water evaporation also the precipitation of the remaining salts happens.

To directly assess desalination effects on the vase, drill powder samples were taken after cleaning, after water bath desalination and after poultice treatment as well. The results can be taken from fig. 7. It is clearly shown that salt concentration in the first centimeter was remarkably depleted after the water bath treatment. At the same time it was increased to the depth, i.e. salts were driven inside by capillary suction during the water bath process. After the poultice treatment the salts have moved back to the surface with capillary transport. A remarkable amount could be removed together with the dry poultice (tab. 2). Given the state of a totally water immersed stone object it will take several month the come into equilibrium with atmospheric humidity again (Franzen & Mirwald 2004). Thus, movement of ions to the surface might still be going on after the poultice treatment.

To evaluate the contribution of water bath desalination and poultice treatment, total content of removed salts was calculated from the measurements and the analysis of the poultice material, respectively. The results are shown in tab. 2. It shows that the water bath treatment with water exchange contributed more than a half of the total mass of salts removed.

Extracted salt quantity	Water bath with daily water exchange (day 1 to 28)	Water bath without water exchange (day 29 to 65)	Cellulose Poultice	Total	
[g]	241	99	108	448	
[%] related to the total content of extracted salts)	53.8	22.1	24.1	100	

Table 2. End result of all desalination measures applied to vase O-12

4. Conclusion

Desalination is a very crucial step in the restoration measure of stone objects. Surface cleaning is to be done prior to desalination for two reasons. External salt deposits should be removed before the wet procedure starts and it is important to "open" the surface to allow water movement. Desalination of stone objects in water bath can easily be monitored by the measuring of the electrical conductivity. The results of the monitoring are used to maintain the measure. The number of water cycles and the duration of each water cycle are decided on the data. The studies have clearly shown that the combination of water bath desalination with a final poultice is the best practice to achieve sustainable results.

5. References

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