

In-situ 'vacuum' desalination - case study of a baroque tombstone

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Abstract

A combined 'vacuum' and poultice desalination procedure was applied to a tombstone made of Cotta sandstone. The desalination steps were controlled analytically by salt profiles in the stone, as well as by analyses of waste water and poultice material. A remarkable reduction of high total salt contents to a depth of 1-2 cm could be achieved, with the best effects in the lower part of the monument (at 50 cm height). In particular, high gypsum contents within the Cotta sandstone were significantly reduced, which could hardly be achieved only by poultice treatments. With respect to the better soluble nitrate compounds, the results are contradictory. Although nitrate could be extracted near the surface, large parts were moved into the stone by advection. The results suggest that the 'vacuum' procedure could be considered as an effective in-situ bath desalination with frequent water exchange rather than a "convective" desalination where the salt ions follow the water streaming through the object. The method has some potential for in-situ desalination of smaller stone objects and should be further developed.

Keywords: desalination techniques, sandstone, negative pressure/underpressure, poultices

1 Introduction

Desalination of salt contaminated objects is an important and common practice in stone restoration. For in-situ conservation measures the most frequently applied technique is desalination with poultices [1]. Recent investigations within an EU-FP 7 funded project [2] helped to better understand the factors controlling the desalination process, such as the pore size distribution within the poultice material related to that of the stone substrate [3]. However, one has to generally accept some limits about efficiency of that procedure, especially with respect to less soluble salts such as gypsum [4]. The alternatives on site to desalination with poultices are scarce.

In the case study presented, such an alternative in-situ approach for smaller objects like sculptures or tombstones started with water circulation and the application of 'vacuum' (negative pressure) of up to 600 mbar on a mainly gypsum-laden sandstone object. The equipment used was modified from the patented vacuum circulation strengthening technique for stone consolidation (VKV = Vakuum-Kreislauf-Verfahren; European Patent no. 1295859, EU ownership hold by Atelier Erich Pummer, Rossatz, Austria). The 'vacuum desalination' was followed by a traditional desalination with a cellulose poultice in the drying stage to additionally take advantage of the drying process and the connected advective transport, as recommended by [5]. To assess the effect of the applied method, a thorough analytical control of the salt content was carried out before, during and after desalination.

2 Materials and methods

2.1 The sandstone object

The sandstone object to be desalinated was a baroque tombstone from a cemetery in Dresden, Saxony (Innerer Neustädter Friedhof, Fig. 1). It consists of a Cotta type Elbe sandstone, a fine to medium grained, clay bearing Cretaceous quartz sandstone (arenite) from the Elbe Valley near Dresden. This sandstone has been a widely used material for buildings and sculptures in Saxony for centuries [6]. Its total porosity of about 20 % is distributed over a broad pore size range. The monumental object shows severe deterioration patterns especially in the lower part of its front side, where the original surface is nearly completely lost. This side has been exposed southwards whereas the back side stood close to a sandstone wall. Although there had been no direct contact between the wall and the tombstone, the small gap in between was filled with mud, rotten leaves, pieces of plaster fallen down from the wall etc. The material in the gap

was permanently wet. For desalination the object was removed from the wall and saved from tipping over by temporarily mounting it on a pedestal.



Figure 1: The baroque tombstone in its original position (left) and from the backside after removing it from the wall and mounting it on a pedestal for desalination (right).

2.2 Equipment and technical procedure

The main principle of the VKV procedure is a deep impregnation of a porous stone material with a liquid by applying an underpressure ('vacuum') to the stone objects. Generally the liquid is a stone consolidant, but due to high salt loads here an adaptation towards a technique for desalination as a first step of restoration was considered. Therefore, the liquid is water.

A schematic sketch of the technical set up and the equipment is given in Fig. 2, while in Fig. 3 different steps of the VKV procedure are illustrated.

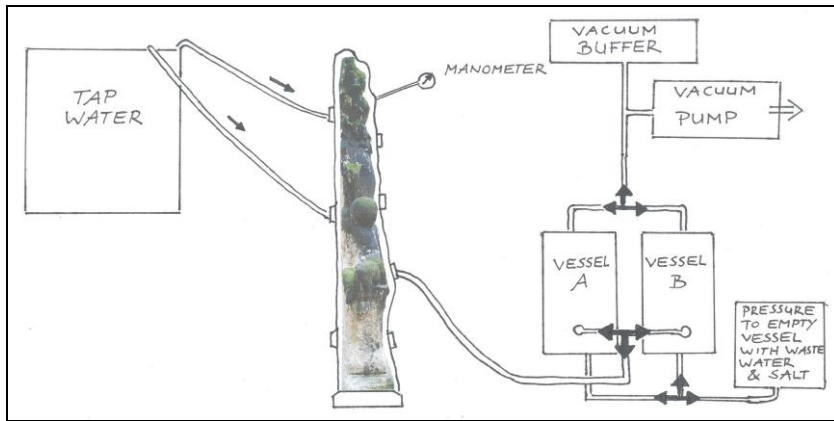


Figure 2: Schematic sketch of the technical set up for vacuum desalination (VKV procedure)

During desalination the object was completely wrapped in a plastic foil which was heat-sealed to isolate it from the surrounding air. The foil bag was fitted with several valves positioned at different heights to be connected with a vacuum pump or with a vessel with water. The sandstone surface of the object right under the foil 'skin' was protected by a highly permeable textile gauze layer to avoid a mechanical stress. By slowly increasing the underpressure via a hose mounted on a valve in the plastic bag, the generously cut plastic foil was moulded perfectly to the object's surface. Maintaining an underpressure of 150-600 mbar within the foil bag for some hours, the air in the stone pores was evacuated. Afterwards, several hoses were attached to the valves at the backside of the tombstone to suck tap water unidirectionally in the foil bag from a big vessel, hereby regularly changing the position of the connections between valves in different positions on the backside and the hoses. The underpressure is maintained during the whole procedure. By opening and closing the valves respectively, fresh tap water could be sucked in from the vessel or tap water with dissolved salt from the object could be sucked off to a smaller vessel. All in all, about 7650 litres of fresh tap water (tempered at 22 °C) were sucked during 7 working days (about 8 hours each day). Overnight the process was stopped, i.e. some water remained in the setup for about 16 hours and was replaced by fresh one again in the next morning. The foil bag was removed on working day eight, and a cellulose poultice was applied immediately after on the entire surface of



Figure 3: The object during the desalination procedure: Protecting the sandstone surface by permeable textile gauze (left), 'vacuum' desalination in progress (middle), and final application of cellulose poultice (right).

the wet object. The poultice remained there for another five weeks. During the drying process the object was sheltered from rain by a roof.

2.3 Analytical control

In a first step, samples (diameter 10 mm) were drilled at three different heights above the ground from the front side as well as from the back side to get information about the salt content and its distribution. Since the thickness of the tombstone is low (22 cm at 50 cm height, 21 cm at 122 cm, and 18 cm at 195 cm), a drilling depth of maximum 10 cm nearly covered a complete cross-section through the object at different heights. The drill powder was weighed on site immediately after sampling and again after drying in the laboratory at 60°C until constant mass was reached. Although there could be side effects due to heat production during drilling, the measured water content in the samples roughly describes the moisture distribution in the sandstone.

Sampling was performed similarly immediately after the 'vacuum desalination' procedure as well as five weeks later after the removal of the poultice. At that time parts of the poultice material (10 x 10 cm each) were also lifted near the drill powder sampling zones to analyze the amount of extracted salts collected in the poultice.

Soluble salts from the drill powder samples and the poultice material were extracted with deionized water. The total salt content of the samples was determined by evaporating the solution and weighing the remaining dry solid matter. Mg, Ca, K, SO₄, Cl, and NO₃ were quantitatively analysed in the aqueous solution by means of a HACH spectrophotometer using standardized reagents. Na was determined with an ion selective electrode. The results were related to the dry sample mass [wt%].

During the first four days of 'vacuum desalination' the salt content of the water sucked off the foil bag was regularly controlled by measuring the electric conductivity several times a day.

3 Results

3.1 Salt contents and salt distribution before desalination

Fig. 4 shows the initial total soluble salt content within the object before desalination. It can be seen that its distribution generally follows a steep profile from the surface to the depth, and the concentration is generally high near the stone surface up to 2 cm. Compared to the back side, concentrations near the surface are significantly higher at the exposed front side.

The moisture content (Fig. 5) is high and nearly equally distributed through the whole cross-section at 50 cm height. At 122 and 195 cm height, moisture content generally decreases with a trend to somewhat dryer surfaces on the front side.

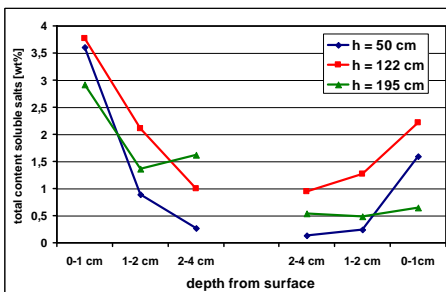


Figure 4: Profile of the total soluble salt content before desalination

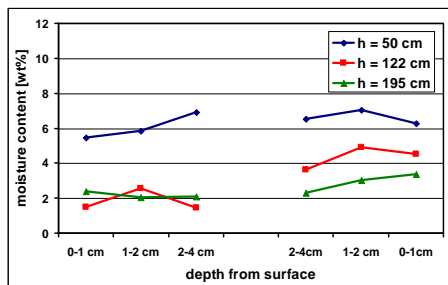


Figure 5: Profile of the moisture content before desalination

This might be due to the free southward exposure of the object at this side, compared to the back side which has been standing against a sandstone wall for decades, with a gap behind, filled with moist material up to a height of about 120 cm (see 2.1). The obtained moisture distribution can be interpreted as a hint towards rising damp from the ground, mainly affecting the lower parts of the object.

The analyses of the single ions show low contents of chloride (< 0.06 wt% in all samples), sodium (< 0.01 wt% in all samples) and potassium (< 0.04 wt% in most of the samples), which are neglected in the further discussion. The distribution of sulphate contents is displayed in Fig. 6. Distribution patterns of sulphate are very similar to those of calcium (Fig. 8) and of the total salt content, which means that gypsum is the predominant salt compound. In addition, remarkable contents of nitrate can be found especially at 122 cm height (Fig. 7). There, its distribution correlates well with magnesium (Fig. 9).

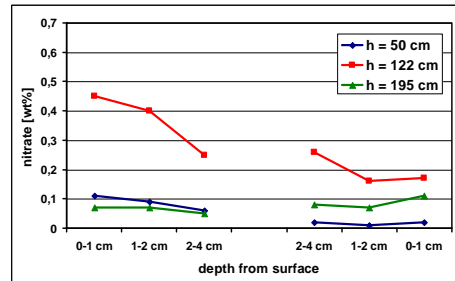
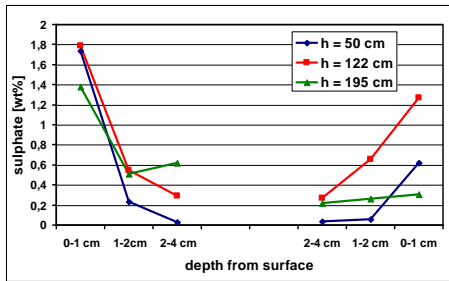


Figure 6: Distribution of sulphate before desalination

Figure 7: Distribution of nitrate before desalination

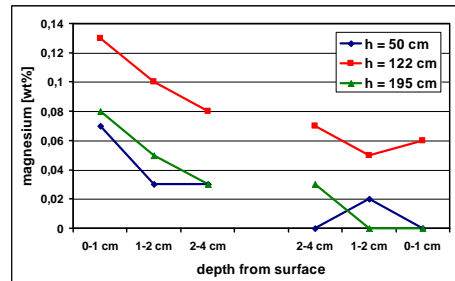
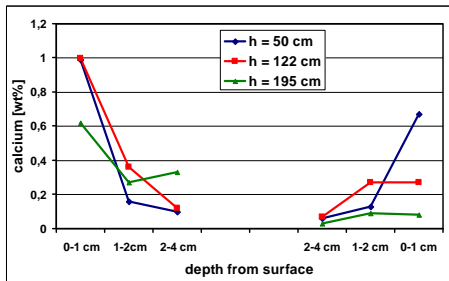


Figure 8: Distribution of calcium before desalination

Figure 9: Distribution of magnesium before desalination

Assessing the salt contents it can be stated that the object is contaminated by a significant amount of gypsum (particularly near the surface, at all heights) and high levels of nitrate (throughout the profile, at 122 cm height). The latter might be attributed to rising damp from the ground, whereas the first is most likely a result of environmental pollution [7]. The salt contents found indicate that desalination is a crucial precondition for a further conservation treatment of the object.

3.2 Salt contents and salt distribution after 'vacuum' desalination

Changes in total soluble salt content after the 7 days 'vacuum' desalination are shown in Fig. 10. The total salt content was reduced in the first two centimetres from the surface; in particular the high contents in the first centimetre were significantly lowered. The best desalination effect can be found at 50 cm height, where the salt content is equally reduced to less than 0.35 wt%. This might be explained by the role of gravity with respect to water movement within the tombstone. As can be seen from Fig. 11, water content of the sandstone at 50 cm height increased to 8-10 wt% in the entire cross-section, which is near saturation of the pore space. Moisture content in the sandstone has increased throughout the object, as can be seen also at heights of 122 and 195 cm, respectively. However, the profile of water content is steeper at these places, indicating that the 'inner core' of the tombstone has not been saturated.

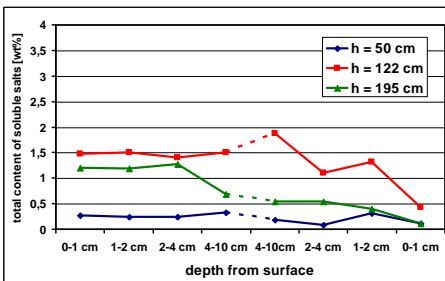


Figure 10: Profile of the total soluble salt content after 'vacuum' desalination

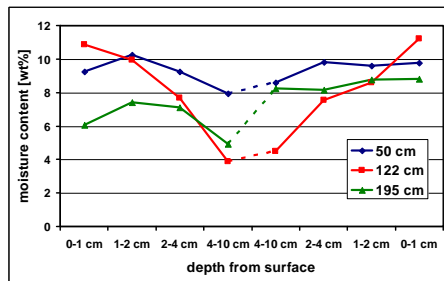


Figure 11: Profile of the moisture content after 'vacuum' desalination

Regarding sulphate and nitrate ions (Figs. 12 and 13), in both cases a significant reduction of contents can be observed near the surface (0-1 cm depth). In case of nitrate, also contents at 2 cm depth are lowered. However, there is an increase of nitrate contents towards the inner core, which might be attributed to the deep penetration of water and the advective transport of dissolved nitrate compounds from surface to the

depth. This can be seen at a height of 122 cm, where the nitrate content is highest.

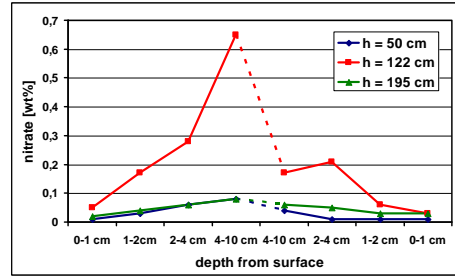
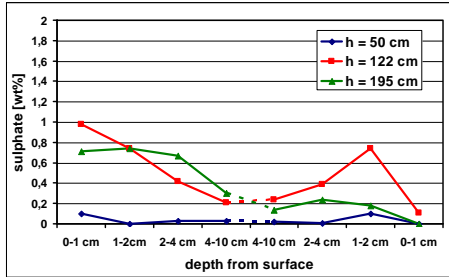


Figure 12: Distribution of sulphates after 'vacuum' desalination

Figure 13: Distribution of nitrates after 'vacuum' desalination

3.3 Salt contents and salt distribution after final poultice treatment

Salt and moisture distribution after 5 weeks final poulticing and drying are displayed in Figs. 14 and 15. Moisture content profiles are comparable to the starting point at 195 cm height or even somewhat lower both at 122 and 50 cm height. It can be concluded that the drying process has finished to a large extent, i.e. the moisture content of the sandstone object is nearly in equilibrium with the surrounding air. The total salt content at 50 cm height has decreased towards zero (< 0.1 wt%, apart from the near-surface sample at the back side with 0.31 wt%). The profile at 122 cm shows an increase of salt contents near the surface and a slight decrease deeper inside; the profile at 195 cm has not changed significantly.

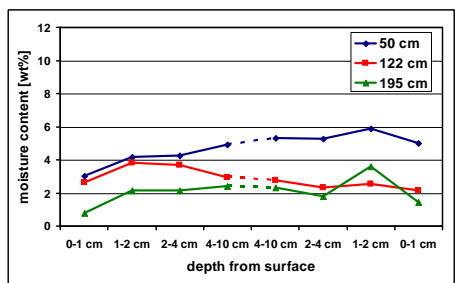
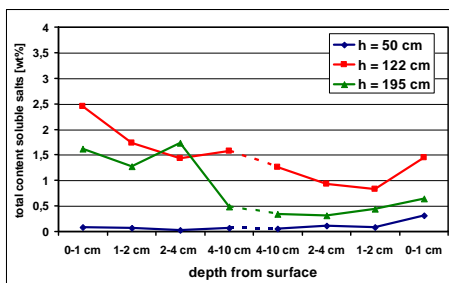


Figure 14: Total soluble salt content after poulticing and drying for 5 weeks

Figure 15: Moisture content profile after poulticing and drying for 5 weeks

Looking at the distribution of sulphate and nitrate, one can see they behave differently. Sulphate is reduced to zero at 50 cm height and shows

a slight, continuous decrease from the surface to the interior at 122 and 195 cm height after poulticing (Fig. 16). The concentrations near the surface (0-2 cm) are significantly reduced, compared to the starting point. Nitrate contents have increased again near the surface but are still high in the interior of the stone (Fig. 17). Likely the penetrating water front has moved highly soluble salts deep inside by advection, but the backward advective transport is interrupted when the sandstone becomes dryer and dryer, resulting in increased ion concentrations in the core and near the surface. Depending on future climatic influences, current distribution of the mobile nitrate might change again towards a more even one.

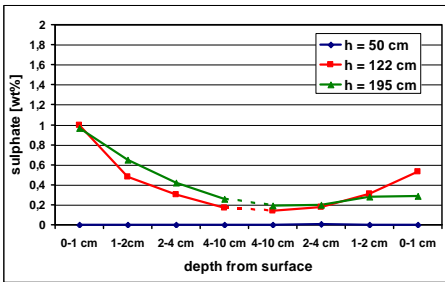


Figure 16: Distribution of sulphate after poulticing and drying for 5 weeks

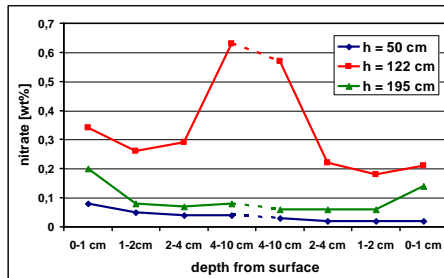


Figure 17: Distribution of nitrate after poulticing and drying for 5 weeks

4 Discussion: Efficiency of desalination and effective mechanisms

4.1 Efficiency of salt extraction

The efficiency of the desalination approach with the combined VKV and cellulose poultice method can be assessed by comparing starting concentrations with those analyzed after the procedure. The results are shown in Figs. 18 and 19. Fig. 18 displays the relative change of total salt concentration in %, with regard to the starting concentration. Since this comparison doesn't provide information about changes of the absolute amount of salt it is completed by another diagram showing the absolute difference between starting and final concentration in weight % (Fig. 19). All in all it can be stated that desalination was most successful in the lower part of the tombstone (at 50 cm height) where the salt concentration could be reduced by more than 80 % at the front side, reaching 4 cm depth. At the back side the effect is somewhat lower. However, the absolute starting concentrations were lower there, too. Bearing in mind that the starting

concentration in the steep profiles was already low at 2-4 cm depth (Fig. 4), a decrease in efficiency towards the inner core does not affect the excellent results. However, the efficiency is significantly lower at heights of 122 and 195 cm. At 122 cm, a reduction by less than 40 % can be found at up to 2 cm depth. At deeper depths the reduction is zero, or even an increase in salt content can be detected (2-4 cm from the front side). At 195 cm height, the salt content near the surface has been reduced by 40 % at the front side, whereas the low concentrations at the back side have not changed significantly.

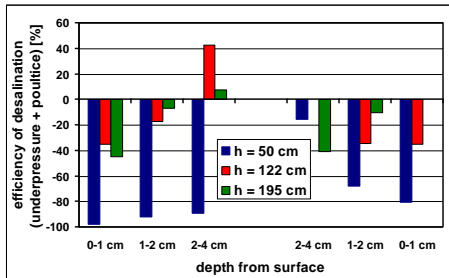


Figure 18: Efficiency of desalination as a function of depth from the surface ('vacuum' desalination + poultice) in %. Negative values indicate a reduction, positive ones an increase of salt content.

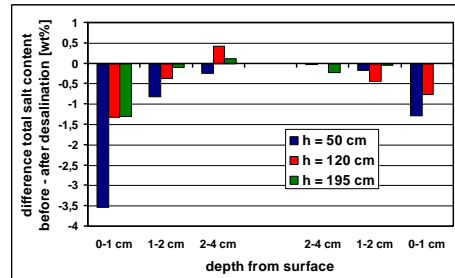


Figure 19: Difference between the total salt content before and after desalination as a function of depth from the surface ('vacuum' desalination + poultice); absolute decrease (negative) / increase (positive) with respect to starting concentration [wt%]

Assessments with regard to the amount of calcium + sulphate (indirectly describing the gypsum content) and nitrate are given in Figs. 20 and 21. It can be demonstrated that the reduction of gypsum worked very well at heights of 50 and 122 cm, down to a depth of 2 cm from surface. Even at greater depths a reasonable reduction can be achieved. At 195 cm high, a contradictory effect can be found at 1-2 cm depth, where the gypsum content slightly increases. However, compared to repeated poultice treatments with cellulose as well as with cellulose-clay-mixtures, the efficiency of gypsum reduction in Cotta type sandstone with the technique applied here is much higher. The gypsum content of sandstone surfaces of the Dresden Zwinger could only be reduced by 25 % at maximum during 3 cycles of poulticing [4].

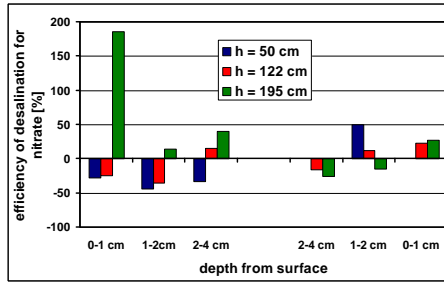
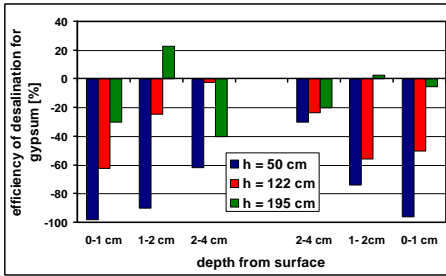


Figure 20: Efficiency of the desalination of gypsum as a function of depth from the surface ('vacuum' desalination + poulticing) in %. Negative values indicate a reduction, positive ones an increase of gypsum content.

Figure 21: Efficiency of nitrate desalination as a function of depth from the surface ('vacuum' desalination + poulticing) in %, with regard to the starting concentration. Negative values indicate a reduction, positive ones an increase of nitrate content.

4.2 Analytical control of waste water

Random samples of 'waste water', i.e. samples of the water sucked off from the foil bag with the object inside, were taken daily during the 'vacuum' desalination process (1.5 litres each). The results (Fig. 22) clearly display the difference between their salt contents during the first day and at the following days. From the second day onward, the total salt content extracted decreased to nearly a quarter of the starting concentration. The concentration of sulphate was continuously decreasing, whereas the (lower) nitrate concentration shows a somewhat higher variation.

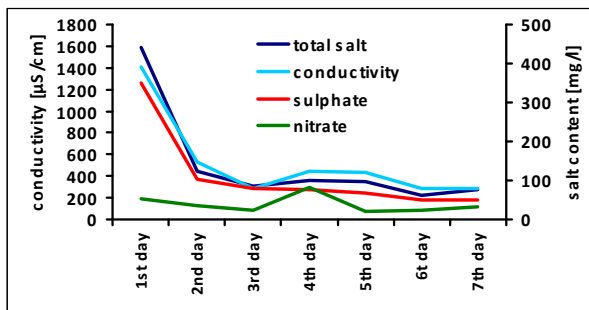


Figure 22: Salt contents and electric conductivity measured on waste water random samples, taken once a day during the entire 'vacuum' desalination procedure

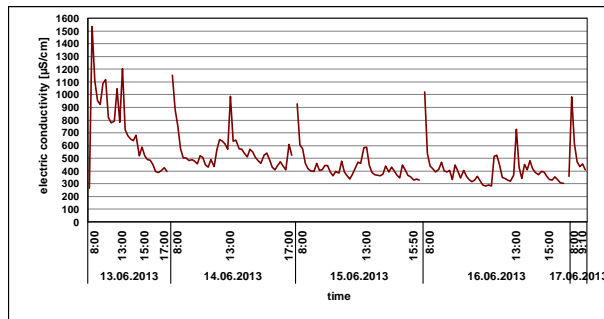


Figure 23: Results of continuous measurements of the electric conductivity of waste water from 'vacuum' desalination

During the first 4 days of 'vacuum' desalination, samples of waste water were regularly controlled by measurements of the electric conductivity. The results are displayed in Fig. 23. According to these results, the extraction of salts was most effective within the first 5 hours of 'vacuum' desalination, when the salts on the surface of the tombstone were dissolved and extracted with the waste water. Afterwards, the concentration was continuously decreasing until the end of the first working day. The repeated increase at the next morning, as well as at the following mornings, can be explained by the longer contact of fresh tap water with the object's surface, allowing transport by diffusion from the outermost parts of the sandstone to the surrounding water. A similar, but reduced effect could be observed daily at 13:00, when the first measurement after the lunch break was done. During the break, the extraction of waste water was temporarily stopped, and the water was longer in contact with the stone surface, which facilitated the diffusion process. The results found are similar to those obtained from conductivity measurements during water bath desalination [5], where the starting ion concentration in the bath was also high and increased again every time after adding fresh water. Consequently, the effective transport mechanism of ions outside the stone during 'vacuum' desalination is due to diffusion. Underpressure is thought to result in a deeper and faster penetration of water into the stone. The fast capillary transport by advection with penetrating water is the cause for the observed backward movement of more soluble salts, such as nitrates, deeper into the stone (cf. Fig. 13). Despite the underpressure applied, the given pore structure of Cotta sandstone with a high amount of smaller capillary pores (between 10 and 0.1 µm) does not allow a fast 'flow' of water through the pore space. Consequently, an outward advective transport of salts only takes place at the drying stage, i.e. during the poultice treatment.

4.3 Analytical control of poultices

Poultice samples taken from the areas near the sampling points for the profiles at 50, 122 and 195 cm height, respectively, were analyzed for their total salt content. The results are shown in Fig. 24. They are in good accordance with the salt profiles obtained from measurements after the final poultice treatment (Fig. 14). The lowest salt contents extracted by the poultice can be found at 195 cm, where the changes in the salt profiles before and after poultice treatment are accordingly low (cf. Figs. 10 and 14). At 50 cm height, where the salt concentration was already very low after the 'vacuum' desalination, the concentration was reduced to nearly zero (Fig. 14). The extraction effect (salt content in the poultice) is remarkable, compared to that at 195 cm, where the remaining salt content in the sandstone is higher. This might be due to the high moisture content throughout the cross-section at this height after the 'vacuum' desalination, which allows even the transport of small amounts of remaining salts from deep inside to the poultice while drying.

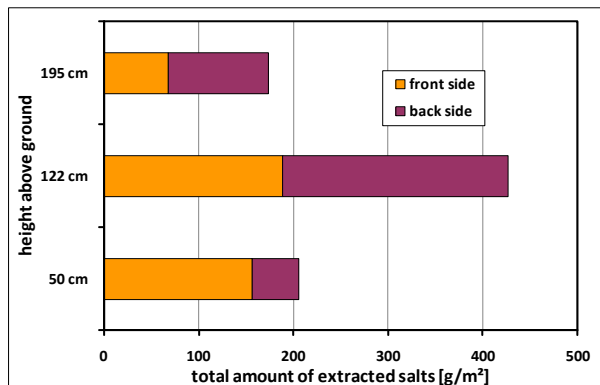


Figure 24: Total salt contents in samples from the cellulose poultice, taken 5 weeks after poultice application at different heights

At 122 cm, the poultice extraction was most efficient. This corresponds well with the high content of highly soluble nitrates in the sandstone at this height (Fig. 17). However, the transport processes had contradictory effects here: while high amounts of nitrates were transported to the stone surface and within the poultice by advection, some nitrates also remained deep inside the object.

5 Conclusions

The applied combination of 'vacuum' desalination and subsequent cellulose poulticing showed good results by reducing the very high gypsum content in Cotta sandstone. Gypsum had been the main salt compound in the treated sandstone object and can be hardly extracted from the Cotta sandstone by usual poultice treatments [4]. Although a reduction of sulphate (gypsum) contents to low / medium levels (referred to WTA Guideline 3-13-01/E [8]) was only achieved at the lower part of the sandstone object, the very high concentrations near the surface could be nearly halved, thus allowing a sustainable further conservation treatment. However, high concentrations of nitrate could not be significantly reduced due to the high mobility of these very soluble compounds. VKV desalination is a promising technical development in restoration. Permanent supervision of the running system ensures safe application. Thus the technical and man power needs are significant. However, it allows a thorough desalination treatment in-situ, which might reduce the risk of and the costs for dismantling and transport of smaller objects. As shown in the discussion about efficiency and the effective mechanisms, the efficiency might be improved by better controlling the dynamic of water change. The results suggest that the procedure could be looked at as effective in-situ bath desalination with frequent water exchange rather than a "convective" desalination where the salt ions follow the water streaming through the object. Moreover, the permanent water stream along the surface is a significant factor which is different to all other desalination methods. Combining the technique with poultice treatments might open new chances for an alternative in-situ desalination method, which could be appropriate especially for the treatment of stone sculptures of high artistic rank.

Acknowledgements

Funding of parts of the project by the German Federal Foundation for the Environment (DBU, Az 30408) is gratefully acknowledged. Thanks are due to Ernst Wandl and Jörn Wichert for technical assistance.

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