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Salt Weathering on Buildings and Stone Sculptures

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Toward an optimization of the specifications for water bath desalination of stone objects

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ABSTRACT

The paper presents some guidelines set up on the basis of the experience gained through desalination of stone objects in water bath conducted in the course of several recent conservation projects. First of all several fundamental questions are tackled: Why to desalinate? What are the variants? What are the risk and the alternative solutions? In a second step, the document proposes general recommendations and reports different methods or techniques that may be used at each step of the process: preliminary measures (diagnosis, salt quantification, stone characterization, pretreatments), artifact positioning into the desalination tank, filling of the tank, monitoring and finalization of the process, bio-contamination risk management, drying conditions, final validation and conditioning of the objects. Finally gaps in nowadays knowledge and desiderata for scientific investigation are pointed out.

Keywords: bath desalination, stone, conservation, guidelines, recommendations

1 INTRODUCTION

Soluble salts are known to be one of the major factors of stone degradation. Extraction of soluble salts is more and more required as a main and commonly preliminary step of stone conservation. Desalination by poultice is undertaken on unmovable stone objects like masonries (Vergès-Belmin & Siedel 2005) whereas water bath desalination is undertaken on stone and other porous inorganic materials, museum objects or recently excavated archaeological pieces, movable items isolated or dismantled from statuary, sculpture or architecture.

Water bath desalination procedure was first described by Rathgen in his 1898 handbook. While not the first to attempt object desalination by water baths, Rathgen, as director of the Chemical Laboratory of the Royal Museums of Berlin, was indeed the first to adopt a rigorous, systematic approach to control the progress of the steeping process by monitoring the chloride and sulphate content of the water bath. He treated one hundred and twenty-five limestone blocks excavated from the Meten Grave Chamber in Egypt and some years later glazed tiles from the Processional Wall and Ishtar Gate of the Palace of Nebuchadnezzar in ancient Babylon. In spite of this early account of what is today generally considered standard conservative method, the intervention remains empirical. It is most often based on the individual experience of the restorer. Indeed, there is no acknowledged and general methodology and most of the specialized literature mainly deals with case studies (e.g. Holbrow et al 1995; Franzen et al. 2008). Few research works have been published and reviews of the state of the art are scarce on desalination (Vergès-Belmin & Bromblet 2001) whereas the mechanisms associated to salt damage are investigated by more and more experiments, models and theoretical approaches in laboratories (Espinosa-Marzal & Scherer 2010; Rodriguez-Navarro & Doehne, 1999; Goudie & Viles 1997).

The following paper has the scope of giving a guideline for the optimization of the procedure which is far from being standardized. Several fundamental questions are raised, such as when and why to desalinate? What are the variants? What are the risks, the alternative solutions? The document also includes recommendations for each step of the desalination process: preliminary measures (diagnosis, salt content…), artifact positioning into the tank, filling of the tank, monitoring and finalization of the process, bio-contamination risk management, drying conditions, final validation and conditioning of the desalinated objects. Finally gaps in actual knowledge and future *desiderata* for scientific investigation are pointed out.

2 DIFFERENT WAYS-TO-DO (WATER BATH MODIFICATIONS)

Usually, desalination is performed by the means of static bath: the stone is simply steeped into successive baths. Nevertheless, various other types of desalinating processes have been carried out to accelerate and optimize the desalination. It has been demonstrated that the daily pumping out of the highest concentrated solution from the bottom of the tank enhances a lot the desalination efficiency (Franzen et al. 2008). Water bath desalination may also be dynamic: the water flows in a close circuit and a device based on electrodialyse (Palem 1996) or a simple deionizing column (Koob & Wong Yee 2000) filters the water and eliminates the extracted salts from the water which is reinjected in the bath. Other alternatives were implemented such as associating bath and poultice, one side being steeped in a bath while the other side was covered with poultices (Siedel 1996). The most original tested methodology was based on electrophoresis principle. The stone is put between 2 electrodes which produce a low electric flow in the bath (Palem 1996). The advantages and drawbacks of the technique have not been actually evaluated (Vergès-Belmin 2000).

3 RISKS OF DESALINATION AND OTHER AVAILABLE SOLUTIONS

Several specific risks for the conservation of the stone object are linked to water bath desalination. Detachment of scales, loss of (remains of) polychromy, dissolution of original parts, damages by swelling, discolouration may occur. Rust of iron parts can swell, break or induce staining. Iron oxides naturally present in some stones can make these material turn yellow after a long time in water. Thus a risk assessment regarding those risks is advised. When tens of comparable pieces have to be desalinated, it is worth adjusting the key parameters of the methodology on only few pieces carefully selected to be representative. When the risk is assessed to be too high because of the fragility and the value of the object, other solutions should be considered. The first one is the desalination by poultice. It has unfortunately only a superficial effect: many experiments have shown that it is impossible to remove salts below few centimetres by poulticing whatever the poultice material used (Sawdy et al. 2008). Poulticing sometimes has relocation effects on the salt distribution in the substrate. Moreover, successive applications and removals of the poultice material may also damage the object surface. Another attractive solution is to control and stabilize the climate (T and RH) around the artwork (Laue 2005). Suitable stable conditions may be determined depending on the salt mixture (Price & Brimblecombe 1994; Nunberg et al. 1996; Price 2000) and maintained in the long term to preserve small and fragile items contaminated by hygroscopic soluble salts inside showcases.

4 GUIDELINES

On the basis of experience collected from several projects including bath desalination of stone, a draft procedure has been established that gives some general recommendations.

4.1 Preliminary measures

When the stone is fragile, preconsolidation of the desintegrated or powdering areas is advised using acrylic resin and/or ethyl silicate. Strips of non woven polyester tissue may be glued using acrylic resins to hold scales and prevent them from detachment.

Loose dust and efflorescences are removed by soft mechanical means (brushing…). It is recommended to take away repairs made of cement, hydraulic lime, plaster of Paris as such materials are capable to supply with salts the water bath during the desalination process. Metallic pieces (iron, rust…) inserted in the material have also to be utterly removed.

Before starting desalination, it is often judicious to quantify the soluble salts content in order to set up the diagnostic and assure the presence of salts which are most often nitrates, sulfates and/or chlorides. Salt contents are analysed on powders sampled by drilling at different depths from the surface. The quantification should be done according to a precise and standard procedure (i.e. Italian standard Doc Normal-13/83 dosaggio dei Sali solubili, 1983, CNR, ICR, German WTA 2001…) in which the way the powder has to be dissolved is specified (time, temperature, powder granulometry…). New powders will be sampled at the end of the process in order to control the decrease of the soluble salts content. In the same way, it is worth knowing intrinsic stone properties such as chemical and mineralogical composition (soluble or swelling minerals?), porosity and capillarity. These properties provide useful information about the general behaviour of the stone material in water: sensitivity, ability to be saturated in a given period of time. Soluble materials such as alabaster, gypsum mortars etc. which are soluble in water can not be desalinated in water bath. In case of suspicion, analyses have to be done to assess the composition of the item.

The question always rises about the actual penetration of the solution to the core of the object. The capillary water penetration coefficient (B expressed in $cm/s^{1/2}$) of the material (see for instance the standard EN15801 (2010) may be used to estimate the water penetration depth. The available data usually characterize fresh material and it is not easy to get test specimens having equivalent properties to the ones of the aged material.

If any painting layers remain, it is important to test the effect of water on them or to perform some analyses to identify their nature. The swelling of the protein layer often present under carnation paints or the solubilisation of “gesso” layers may induce dramatic loss of paintings that should have been preserved. Armenian bole under metallic leaves is also very sensitive to water. Furthermore it is important to keep in mind that epigenic gypsum layers should be preserved as they are now a part of the original object, when sulphates have partly replaced carbonates just beneath the surface of calcareous stone (Bromblet & Vergès-Belmin 1996). If some treatments previously applied to protect or to consolidate the stone are suspected, it is necessary to put them in evidence and to anticipate any difficulty that they might induce in the course of the desalination. For example, impervious protective layer applied in the past such as bee wax that could prevent the water suction within the stone can be dissolved and removed by an appropriate solvent. However, objects can be desalinated in spite of a hydrophobic superficial layer and in few cases objects have been treated with water repellent by restorers in order to avoid swelling (i.e. earth plates) and damaging in water bath (Lefèvre & Pre 1996).

4.2 Artifact positioning in the desalination tank

In order to avoid handling heavy and finely sculpted blocs in wet state, draining tanks or a pumping system to change water are used. The dimension of the tank has to be adjusted to the size and the volume of the stone which must keep totally immersed all over the time of the bath. Thus the tank (wooden frame lined with foil or foil lined wood/metal/plastic containers) is often specifically arranged around the object. Of course, it is necessary to use a tank larger than the stone but not too much larger. A huge volume of water makes it difficult the detection and quantification of the amount of salts extracted from the stone. It would take a very long time to reach the stage in the curve of conductivity used to monitor the desalination process (see 4.4). It would also increase the risk of microbiological activity to take place. There is not an agreement on what is the best ratio water/stone volume and it ranges currently from 1/1 to 15/1. Some conservators use one single very long lasting bath while others rather use successive short time baths to avoid any risk of uncontrolled biological growth.

Stone should not be laid directly down on the bottom of the tank but raised on pieces of autoclaved wood, plastic cleat, extruded polystyrene or polyethylene foam to facilitate water circulation at the lower face of the blocs. It is better to arrange in groups only objects which show comparable volume and degree of decay. It is useful to cover the bottom of the tank with a dark liner to help anyone to visualize any loss of material during the immersion.

4.3 Filling of the tank

Water should be pure and clear. Demineralised water is recommended. Tap water has been used to save money and to reduce the cost in archaeological sites in remote locations (Holbrow et al. 1995). Its quality has to be confirmed first and in any case demineralised water has to be used for the last baths. Distilled water is too expensive and probably too aggressive, thus not recommended. The tank is filled by pouring water very progressively and not directly on the object to achieve a good capillary saturation of the porous network

4.4 Monitoring and finalization of the process

The monitoring is based on the measurement of the conductivity of the solution with a calibrated conductimeter. Specific electrodes dedicated to one single ion (chlorides, nitrates or sulfates) may be used (Fig.1) to follow the extraction rate of some particular salt species and compare it to the evolution of the conductivity. In the case of a static bath where water is neither partially renewed nor treated by any deionizing system, conductivity of the solution increases with its salt content before reaching a stage where the extraction rate becomes very low. The solution is not any more efficient to dissolve and extract salt. The extraction process is mainly a diffusion process. It is useless to keep the stone into a bath if the desalination rate is too low. It is then recommended to replace the water by fresh water. Chlorides and nitrates are usually responsible for a first important step, in particular in the first baths. But it is necessary to keep on until the dissolution of less soluble sulfates takes place (Fig.1). It is important to measure the conductivity at the same place, depth and temperature or to homogenize the solution by stirring before the measurement because salts are not homogeneously distributed within the bath. They concentrate at the bottom of the tank due to gravity. The evolution of the state of the stone has to be controlled at regular intervals in particular in degraded areas. No method other than visual examination have been proposed to monitor possible side effects like dissolution, erosion etc. that may take place during the operation (Holbrow et al. 1995). It is possible to accelerate and to homogenize the salt extraction action by diving water pumps to create a flow all around the object. This mechanical stirring has to be controlled and is not systematically suitable as it was reported to lead to erosion in case of fragile ceramic bodies (Costa Pessoa et al. 1996).

No agreement has been reached on the optimal duration of the drying phase between two successive baths. Short duration allows a good continuity of the desalination process from one bath to the following one as the porous media remains saturated with water. It prevents any salt crystallization. In case of very capillary material, as the inner saline solution is transported toward the surface by capillarity during this drying phase, a longer duration could improve the salt extraction when the new bath starts at the condition that the capillary absorption and the re-saturation of the material do not counteract this effect.

4.5 Desalination completion

Desalination is considered to be achieved as soon as water conductivity is close to the one of the fresh water used when the steady state is reached in the bath. It is possible to use a blank bath with the same fresh water and a stone of the same quality but without any soluble salt to obtain the conductivity that should be reached. Through case studies review, one bath may last between 5 to 20 days and 5 to 15 baths are usually necessary to extract salts present in depth from objects weighing 30 to 100 kg. It is necessary to be aware that water bath desalination may take many months before starting a conservation process including such an operation.

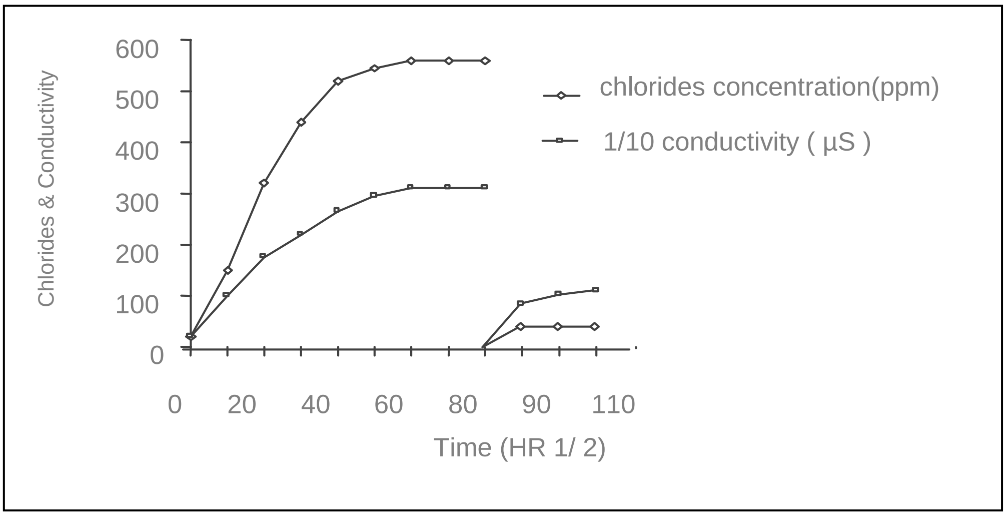

Figure 1. Control of a bath desalination of bricks through conductivity and chloride contents measurements. During the second bath, chloride content reaches an asymptote, while the conductivity continues to increase because other less soluble salts are mobilized (after MacLeod & Davies 1987).

4.6 Bio-contamination risk management

In order to avoid bio-contamination and the use of biocides (the most common ones, quaternary ammonium based, contain soluble anions such as chlorides), it is necessary to maintain the bath in darkness and to protect it from dust by covering the tank. It is usually sufficient to prevent green algae growth. Cleaning up the tank after each bath with a wet sponge and working at low temperature (10 to 15°C) help also to prevent biological colonisation. High nitrate content in the material promotes a thick brownish film formation within few hours if the water has not been changed before. A transparent plastic film is sometimes put at the surface of the bath to reduce the oxygenation of the water and thus the biological growth (not valid for anaerobic microorganisms). The efficiency of such a method has still to be demonstrated. It has been suggested to create a water circulation with UV lighting, a powerful biocide agent. The method is supposed to be effective…

4.7 Drying conditions

At the end of the desalination, the stone has to dry for one to few months according its volume, thickness and petrophysical characteristics at ambient temperature and humidity (RH). Using elevated temperatures or ventilation to accelerate this phase requires a great attention. Temperature and humidity should be measured and registered to know the environmental conditions in which the object has been stabilized before leaving the workshop. A poultice is sometimes applied to absorb the last salts and the brown products (supposedly organic matter) which may soil the stone during the drying phase. Remarkable amount of residual salts can be removed with the poultice once it has dried (Franzen et al. 2008). It is necessary to verify that no biological activity occurs under and within the poultices while it dries.

4.8 Final validation and conditioning of the desalinated dried objects

The drying state of the stone could be monitored by daily weighing until it reaches a stable mass (less than 0.1% of variation in 24h), but the weigh of the object is not always compatible with the scale of the balance available at the workshop or in the laboratory! The use of a humidimeter provides only relative and indirect information on the superficial water content of the material.

The ending of the water bath desalination does not constitute a blanket endorsement for the future conservation of the object. It is recommended to make new quantification of soluble salts on few dried and stabilized pieces. Powders are collected by drilling close to the sampling done just before the desalination, at the same depths. Quantification has to be done according the same procedure in the same laboratory to be comparable and to allow the complete validation of the desalination performance. Many cases have been reported where unexpected residual contents in sodium chlorides or sulfates (thenardite, mirabilite) or in magnesium sulfates (hexahydrite/epsomite) were responsible for new degradation whatever the conservation place of the object: outdoor, inside a museum and even under the protection of a showcase! It is noticeable that desalination to be effective has to decrease the salt content at the surface but also in depth. The threshold value is around 0.1% for chlorides, nitrates and sulphates if sodium or magnesium sulphates are suspected (WTA 2001; Multiauthors 2003). It is recommended to survey the evolution of the stone surface for one year after the end of the operation and to pay attention to any efflorescence, powdering, scaling phenomena that indicate the initialization of a new salt weathering process.

After drying, consolidation with ethyl silicate is usually performed under the justification that the desalination has weakened the material. This treatment may increase the decay in presence of salts. It should not be applied systematically but only on restricted weakened areas. As soluble salts are no longer present in harmful proportions inside the material, desalinated stones may be stored or exposed at room temperature and humidity without any risk. It is not at all necessary to ask for a temperature and humidity regulated showcase to preserve artwork correctly desalinated.

5 WATER BATH DESALINATION OF STONE OBJECTS: TOWARD AN OPTIMIZATION OF THE SPECIFICATIONS

Water bath desalination is not a new practice and it is more and more required as an important preliminary step for stone conservation. Nevertheless desalination remains a delicate intervention for which it is difficult to plan in advance any precise duration and number of baths required. Monitoring by conductivity measurements enables to determine the duration of each bath and the total duration of the desalination. It is necessary to reach residual soluble salt contents beneath the threshold values published in the literature in the object in order to avoid any new salt weathering after the treatment. Many parameters have to be taken into account to optimize the desalination in terms of efficiency, harmfulness, duration and cost. New techniques (electrophoresis) which have not been completely and scientifically evaluated with their drawbacks and advantages have been used from time to time. They require more research work before being extensively promoted.

In conservation workshops, as no recognised procedure is available, the desalination intervention is very different from one conservator to the other and many variants have been introduced at each step of the process. Practices which seem ingenious or questionable have to be evaluated by scientific experimentation to know their actual impact. Research projects have to be encouraged to create new tools for evaluating the efficiency and the harmfulness of bath desalination. Mathematical models would be helpful to know the water penetration depth and soluble salts mobility as a function of time taking into account the physical properties as well as the dimensions of the stone material. In the same way, drying conditions could be more precisely estimated using water permeability models. The thorough control and quantification of any modification of the surface of the object during and after the end of the treatment suffer from a lack of available tool and methodology. Chemical investigations (calcium or silicium quantification in the water) and microtopographic measurements would likely be helpful.

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