Diagnostic investigations to define the possibility and the effectiveness of desalination with the poultice-technique – a case study

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Abstract

The contamination of the walls, especially the surfaces with salt and a salt solution is often one of the biggest problems concerning the conservation concept of wall paintings. A good example for that is the Cathedral in Königslutter in Northern Germany.

The wall paintings of the Cathedral in Königslutter go back to a medieval wall painting, which was painted over at the end of the 19th century. In the second half of the 20th century large amounts of cement suspension were injected into the walls to stabilize the static of the building, which started the damaging process essentially by salt crystallisation at the inner surfaces of the cathedral. After the outbuilding was completely repaired in 2006 the conservation of the wall paintings, plasters etc. in the cathedral begun.

The analyses of surface samples and the drill - sampling show a high salt content consisting of sulphate and calcium ions, nitrates (mostly together with potassium but also with calcium) and rarely chloride and sodium. Salt efflorescences are often made of gypsum partially together with Calcite as a sinter crust. Fluffy efflorescences consist of niter. The total amount of salt only in some cases decrease with the depth of sampling.

To extract the salts in the wall painting and in the plaster the poultice method was chosen. Before applying this method the surfaces have to comply with the requirements for a successful application e.g. the moisture transport characteristics. The results show clearly that the first plaster layer, which is slightly hydrophobic in some parts, very slowly transported moisture. Despite the low moisture transport rates the poultice method was tested, because salt action is the most damaging process. The application tests show that only a small amount of salt can be extracted.

Keyword

Desalination, wall painting, Mirowski method, droplet method, poultice.

1. Introduction

The wall paintings of the cathedral in Königslutter date back to the 13th century. As many other wall paintings of that age they were altered and underwent changing conditions regarding physical, chemical and biological influences. Presumably from the 16th until the end of the 19th century a whitewash covered them. In the years 1886-1894 the wall paintings were uncovered and restored in the sense of that time by Essenwein and Quensen (Königfeld 1996; Grote & van der Ploeg 2001), i.e. that the medieval surface was nearly completely over painted.

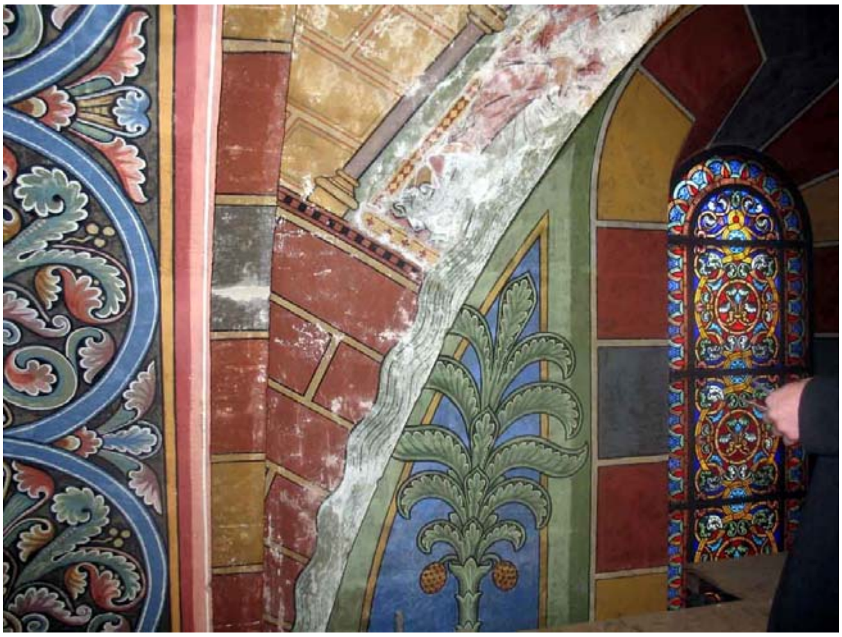

Figure 1. Salt damage of the wall paintings in the cathedral in Königslutter

In 1974 large amounts of cement suspensions were injected into the walls to stabilize the static of the building. The wall paintings were previously treated with an acrylic resin in order to protect the surface. However while the static consolidation succeeded the protection of the wall paintings failed. Comprehensive diagnostic investigations started around 1990 and it was evident that as a consequence of the injected suspension the masonry was intensively penetrated with moisture. The damaging process was essentially caused by the mobilisation and the crystallisation of salts (Rösch 1996).

On the basis of these results a long-term concept for the preservation of the cathedral including the conservation and restoration of the wall paintings was developed by an interdisciplinary group of experts. The already necessary reparation of the outbuilding was performed until 2006 as the first step. This was combined with the stabilisation of the climate in the interior of the building particularly with respect to the relative humidity. Furthermore the effectiveness of these measures was controlled since 2003 by the monitoring of representative areas of the surface (Behrens et al. 2005). The photographic monitoring was combined with a variety of non-destructive diagnostic investigations and with a limited number of samples for chemical analysis.

On the one hand it could be confirmed that the damaging process was substantially reduced. On the other hand when looking to the contamination of the walls with salt and salt solutions, it was of utmost importance to establish whether the desalination or at least the reduction of salt contents is possible or not. This paper is focused on diagnostic investigations in order to characterize selected areas and to estimate the effectiveness of the desalination with the poultice-technique. For this purpose it was necessary to determine the exact content oft the salts, the distribution of the different ions and the salt minerals which could form depending on the climatic parameters. Alike important were the hygric properties of the materials regarding the capillary transport of moisture as well as the diffusion of water vapour (Niemeyer & Stadlbauer 1996).

2. Experimental

2.1 Methods

Quantitative chemical analyses

By measuring the conductivity of the aqueous extract of the samples, the total amount of salt could be estimated.. The quantitative determination of Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-} was carried out by photometry and a Na - selective electrode.

XRD Analyses of mineral phases

By X-ray diffraction (XRD) the mineral phases were analysed on powder samples by a Bruker D4 Endeavor.

Salt screening with the Polarising Microscope (PM)

With the polarising microscope (Zeiss Axioplan 50) the aqueous extracts of a sample after drying on a microscope slide were analysed for salt phases and the hygroscopic behaviour of the salt system.

Water uptake with the method of Mirowski

The method after Mirowski was used to measure the capillary uptake of water surfaces, i.e. the hydrophobic / hydrophilic properties. The water is offered the surface by an on one side closed glass tube with a sponge on the other end. The greater the suction value of a surface the more water is taken up out of the cylinder. Surface points, which show hydrophobic with the droplet method, are not further studied with the Mirowski method.

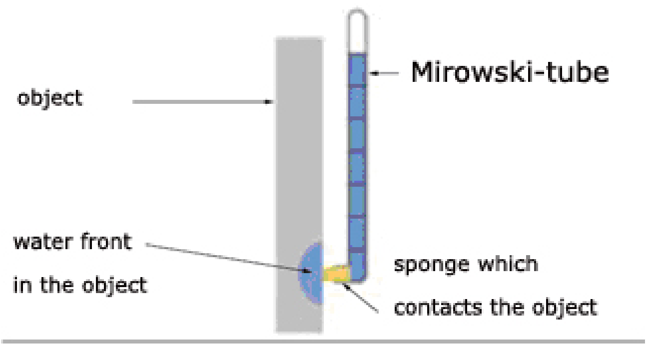

Figure 2: Sketch of the Mirowski method

Figure 3: The droplet method

Determination of the absorption of water with the droplet method
With the droplet method around 10 µl of water were offered to the surface which has to be tested. The time until total absorption of the water droplet is a quantitative measure of the water absorption velocity i.e. the hydrophobic / hydrophilic properties.

2.2 Samples, Measuring points

Two model areas were chosen for testing the poultice method. Before and after applying the poultices, samples up to 10 cm in depth were taken with a spiral drill (1cm Ø) analysed for salt ions.

Before the application of the poultices in the model areas 22 samples were analysed quantitatively for their ions and 18 samples, which are salt efflorescences and other surface samples from different locations, were analysed for the salt phases and the hygroscopic behaviour of the salt system. After the application of the poultices 12 samples from these areas were taken to estimate the effectiveness of the desalting process.

To characterise the moisture transport at the surfaces on the points in each model area measurements with the Mirowski-tube were carried out. The droplet method was applied at more than 40 places for each model area.

2.3 Poultices

Three recipes were used:

- Recipe 1 "wet": 20g poultice mixture 1:1 (Arbocel® 200 und Arbocel® 1000) and 168 ml deionised water.
- Recipe 2 "let dry I: 20g poultice mixture 1:1 (Arbocel® 200 und Arbocel® 1000) and 129 ml deionised water with an intermediate layer of Japanese paper.
- Recipe 3 "let dry II": 20g poultice mixture 1:1 (Arbocel® 200 und Arbocel® 1000) and 127 ml deionised water without an intermediate layer of Japanese paper.

3. Results and discussion

3.1 Salts in the plaster and at the surface

The results of the analyses of salts and salt forming ions are:

- In all sampled areas on or near the surfaces the amount of salt found is very high.
- The salt composition consists mostly of sulphate and calcium (fig. 4), in some areas nitrates (with potassium but also calcium as the counter ion). Only in very few cases sodium and chloride were found.
- The white powdery efflorescences are made of gypsum and sometimes of calcite too (sinter crust).
- The fluffy whiskers consist of niter (KNO_3).
- The salt content is often not really decreasing with the depth of sampling.

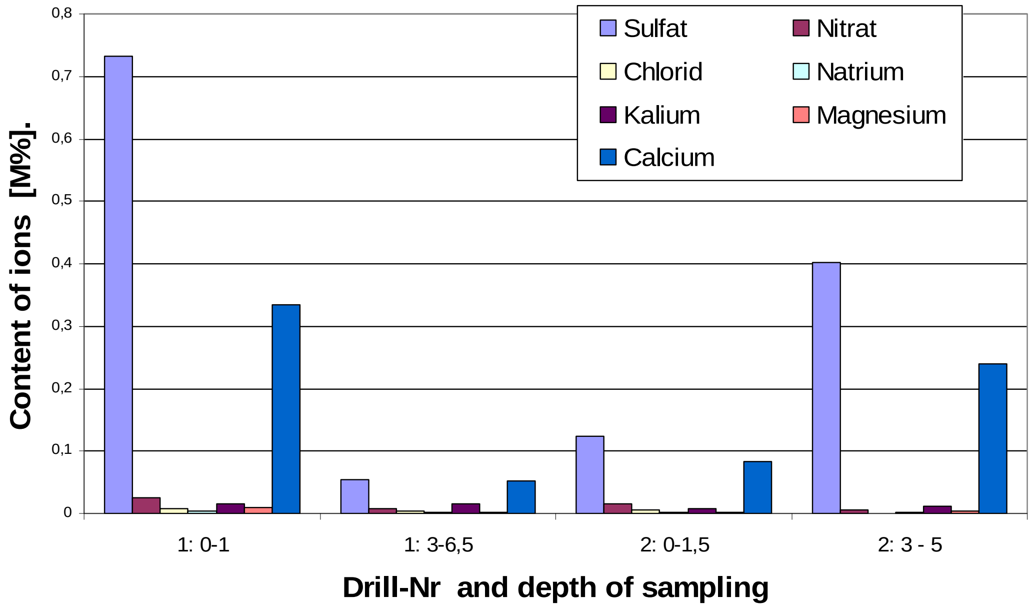

Figure 4: Gypsum dominated samples

Considering the fact that the salt content is not decreasing substantially with depth it can not be expected that salt reducing measures could lower the salt content to an sufficient level to avoid further salt damage.
But the salts near the surface especially the gypsum should be removed. Salts like niter should be easily be reduced near the surface with the poultice-method, whereas gypsum except for the very powdery forms has to bring in solution before with an appropriate method.
On the other hand salts like niter will easier than gypsum migrate again to the surface, which could be observed at places on a new repair mortar, where after some days thin needles of niter are visible.

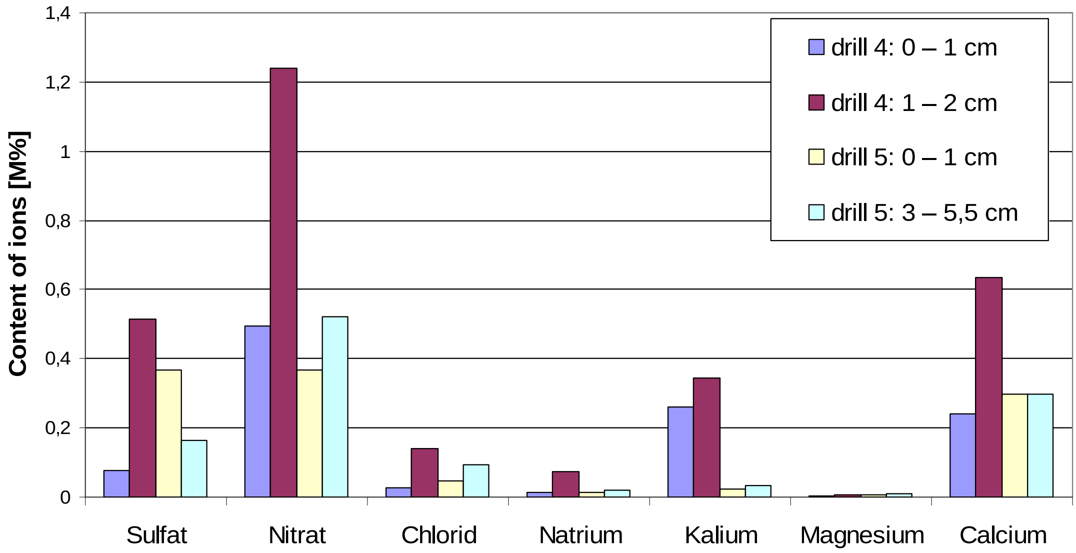

Figure 5: Niter and nitrates dominated samples

3.2 Water uptake by the surfaces of the wall paintings

The uptake of water by capillary sorption is low to very low. With the Mirowsky method values of about 0,8 ml/h are measured.
The greatest water absorption show surface defects and gilded areas but only sometimes the 10µl droplet is taken up in a few seconds. Most it takes 1 –10 minutes. In some places e.g. the green regions in the "SO Fluss" the droplets were visible even at more than 40 minutes (hydrophobic surface).

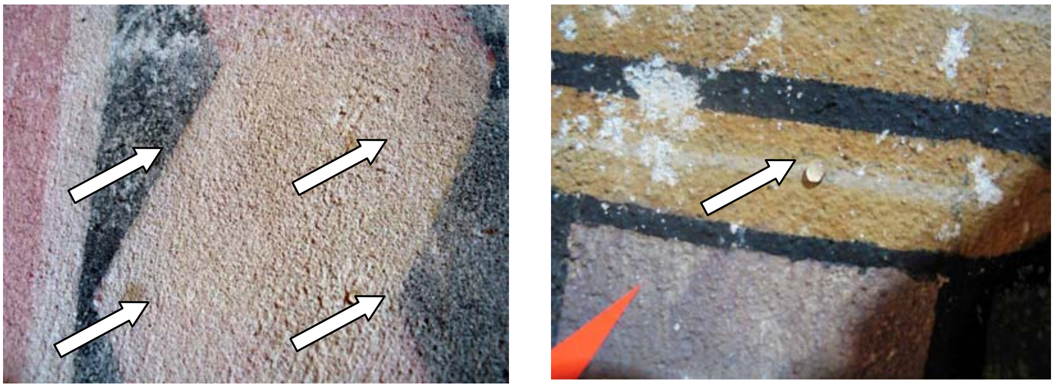

Figure 6: The droplet method was used for 15-20 measurements for each model area

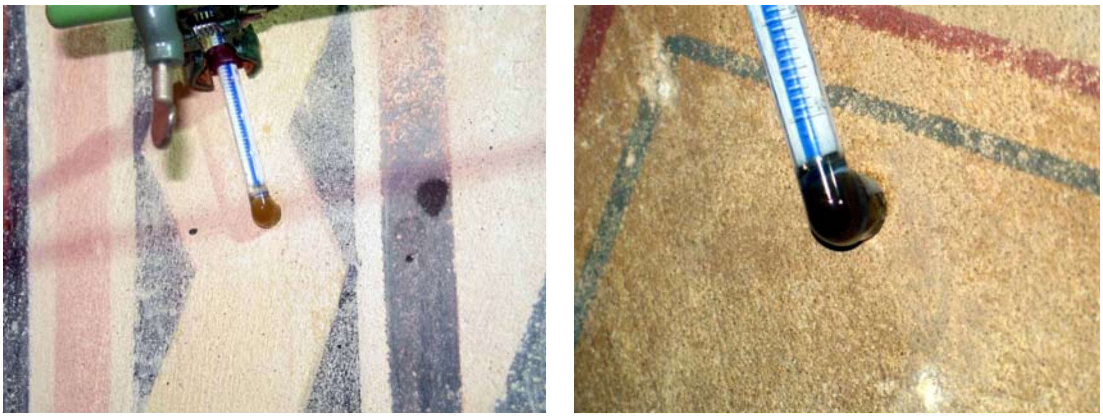

Figure 7: Measurements with the Mirowski method were carried out in two places for each model area.

Studies with the droplet method were also carried out on samples of the plaster layers, which can be divided in a first and a second layer. The first layer shows always very low water absorption, whereas the second plaster layer always immediately incorporated the droplet in the structure. The first layer shows the effect of low water suction on both sides of a sample.

Looking to a possible salt reduction by cellulose poultices, these results are a very bad precondition for this type of salt reduction method. This means, that only minor amounts of salt could be solved and get into the poultice. But because salt damage is the major damaging factor, the method was checked in more detail.

3.3 Testing the salt reducing method

The salt reducing methods are applied and verified on two areas in the vault of the cathedral with different salt systems.

Figure 8: Model areas with cellulose poultice in the „NW Fluss“ (left) and in the S-transept.

Three recipes were tested using a step by step application of the cellulose poultice. The first poultice was applied for a very short time (2-3 minutes) followed by a second poultice layer which should dry out and take up any dissolved salts from below. As a first result only the poultices without a layer of japanese paper did not fell off and could dry out in place.

3.4 Analyses of salts in the poultices and the surfaces below

To assess the results of the measures in the model areas, the poultices after drying, a neutral poultice (with just the starting materials) as well as again drill dust samples from the areas which were sampled before and which now represent the salt content after the application of the poultices, were analysed. The sampling with a twist drill took place in short depth dependent segments to distinguish the first and second layers of the plaster.

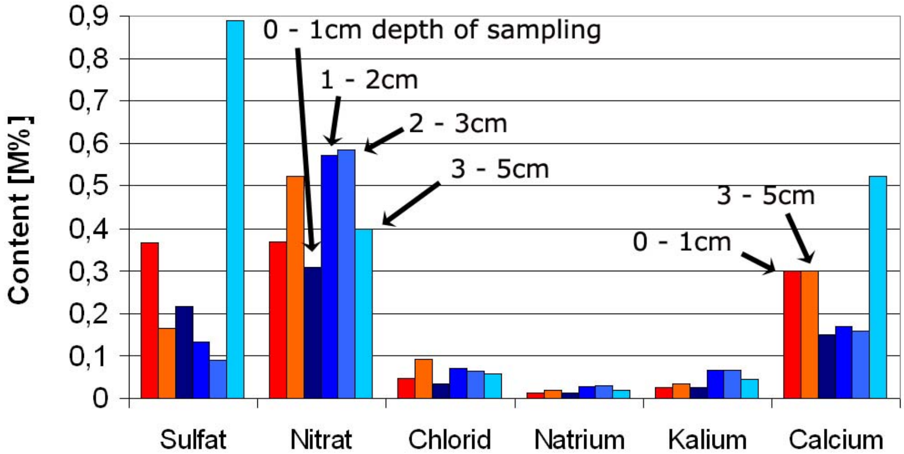

Figure 9: S-transept : Distribution of salt forming ions with depth of sampling before (red columns) after salt reduction (blue columns).

Looking to the final results of the analyses a clear success of the salt reducing methods could not be found.
In the first centimetre a slightly reduction of the salt content could be found, but looking to deeper regions in the plaster nearly no salt extraction could be observed (fig. 9, 10).

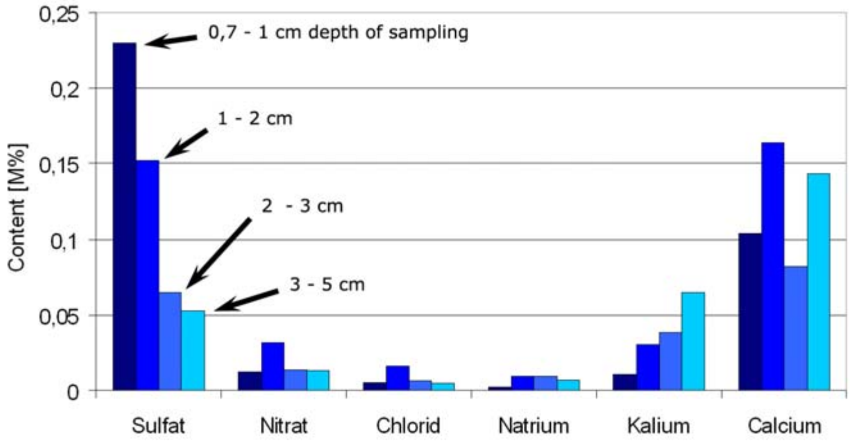

Figure 10: Distribution of salt forming ions with depth of sampling after salt reduction in the test area "NW-Fluss". A decrease can only be observed with the good soluble salts made of Na^+, K^+, Cl^-, NO_3^-.

Especially clear becomes the effect of the salt reducing measures looking to the total amounts of the extracted salts in comparison with the starting values in the plasters.
In the first centimetre of the surface in the SW corner of the S-transept 170g salt/m² were found while by the short time poultices only about 1g salt/m² and the drying poultice about 5g salt/m² (fig. 11) could be extracted, mostly very soluble salts and not gypsum.

In the first centimetre of the surfaces of the „NW-Fluss" of the choir vault about 100g salt/m² were analysed. The short time poultice has extracted 0,5g salt/m² and the drying poultice about 2g salt/m².

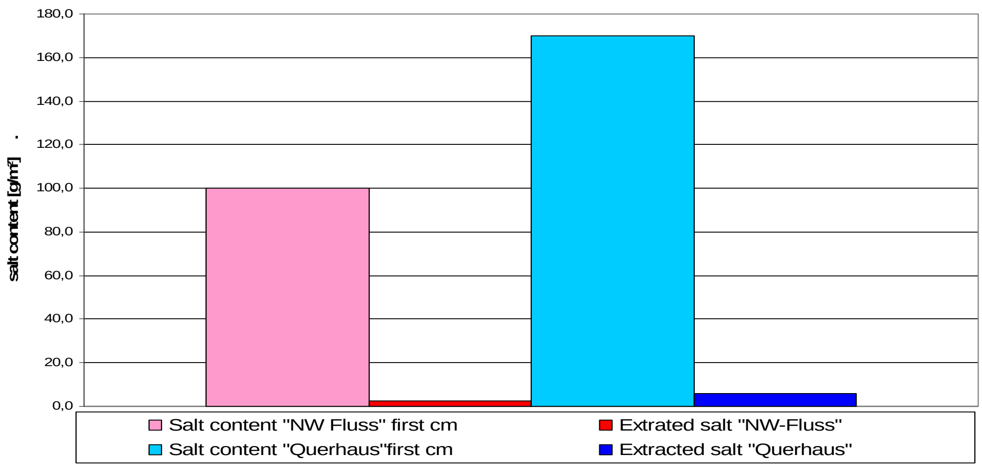

Figure 11: The efficiency of the salt reducing methods at the two model areas.

All together with the applied methods only 5% of the salts could be extracted. The poultices do not reach depths of more than 1 cm.

3.5 Simulation calculation of the sequence of crystallisation

Using the software RUNSALT/ECOS (Price 2001) starting with the quantitative results of our samples the possible sequences of crystallisation were calculated depending on relative humidity and air temperature.

Before the desalting procedures Gypsum is always the first salt appearing but it has to be extracted from the input data. The first plaster layer shows after this crystallisation of gypsum a sequence of sulphate bearing double salts starting at about more than 90% RH. This means that salt crystallisation takes place in any case in the cathedral. The second plaster layer from the same location shows in the simulation salt crystallisations beginning at about 80% RH with nitrates of potassium and sodium.

After the salt reducing testes two samples were taken at the “NW-Fluss”. Both show a calculated begin of salt crystallization at about 80% RH with KNO_3 as the most important salt besides the omnipresent gypsum.
The test areas at the S-transept show after the desalting a calculated salt system starting crystallisation just below 40% RH which means that in addition to gypsum no other salt will crystallize in the actual climate of the cathedral.

4. Conclusions

The results of investigations of surface samples and drill-sampling up to 10cm depth show a high salt content consisting of sulphate and calcium ions, considerable amounts of nitrate (mostly together with potassium but also with calcium) and rarely chloride and sodium ions. A great deal of the salt efflorescences is often made of gypsum partially together with calcite as a kind of sinter crust. Fluffy efflorescences consist of niter. The total amount of salt only in some cases decrease with the depth of sampling.

While salt efflorescences could be easily be removed dry, to extract the salts and salt forming ions in the wall painting and in the plaster the poultice method was chosen. Before applying this method the surfaces have to comply with the requirements for a successful application especially the moisture transport characteristics. The results show clearly that the first plaster layer very slowly transports moisture, which means that it is slightly hydrophobic. This is not a good condition for applying the poultice method.

The result of the application tests show that only a small amount of salts can be extracted. Altogether less than 5% of the total amount of salt can be removed which means that the method as tested is not promising.

Because of the low efficiency of the tested method it should not be applied in this way. An appreciable efficiency in the depth is not given because of the low capillary water suction characteristics of the first plaster layer in many parts of the surface.

Besides the dry removal of the visible salts the recommendation for desalination, as the result of our investigations is that the salts near the surface should be removed by application of one thin poultice in combination with a controlled climate. By

application of a single not too wet poultice a great deal of these salts can be removed. After drying the near surface salts can be taken off. Although not a great amount of salts will be removed, the surface of the wall paintings will be better prepared for all further applications e.g. retouching and any salt damage will probably delayed for some time.
The investigations have again clearly shown that before salt removal poultices were used the water transport rate and hydrophobic/hydrophilic properties of the underlying plasters should be known.

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