
**Terracotta at Schloß Schwerin, Different Desalination Treatments
for the Application of Stone Consolidating Agents**

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1 ABSTRACT

At Schloß Schwerin in northern Germany terracotta relief plates used for the decoration of the outer facades show various degrees of degradation. It is planned to develop a sustainable restoration concept for terracotta plates including a treatment with stone consolidating agents. A high gypsum content of 3-10 % within the upper layer of the plates seems to be the main reason of decay and responsible for the loss of the sintered surface of the plates. Furthermore, the gypsum content would prevent the effective uptake of stone consolidants because the pores responsible for capillary transport are blocked.

To prevent further damage and for a successful treatment with stone consolidating agents desalination was necessary. Two poultice desalination techniques were tested. The first was a treatment with deionized water aiming at the washout of gypsum from capillary active pores. Secondly, poultices with ammonium carbonate solution used for the transformation of gypsum into easily soluble ammonium sulphate were applied.

The effect of both procedures was verified by analysis of salt profiles before and after the treatment as well as by the soluble salts content in the poultices. Changes in the capillary uptake of the material were detected by Karsten tube measurements.

2 INTRODUCTION

Architectural elements of terracotta were widely used for building decoration in northern Europe. This material plays a decisive role in history of art of the renaissance and historicism style in northern Germany.

The last major restoration and reconstruction of Schloß Schwerin was carried out between 1845 and 1851. Terracotta plates used for the decoration of the outer facades dated from that time. In the brickworks moulds were used for the preparation of these decorative plates. The burning procedure lead to a typical smooth surface of sintered clay compounds in the uppermost layer of the plates.

Typical damages of the terracotta plates are black discoloration and material loss because of sanding off as well as the detachment of small scales. For the deterioration the loss of the sintered surface seems to be the most important and initial step for further degradation. As observed by light microscopy and SEM gypsum filled gaps and cracks parallel to the surface seem to be of high relevance for this process (SCHLÜTTER *et al.*, 1994). After the loss of the surface the degradation within the smoother material underneath increases.

For terracotta used on outer facades the enrichment of salts is one of the most important factors for decay. If rising damp is neglected rain water intrusion by direct or indirect impact of precipitation and dry deposition of gases and particles from the atmosphere are the most important sources for salt enrichment. Crystallisation and the change of physical properties of the salt contaminated areas are responsible for the weakening and degradation of the material. Gypsum accumulation in the first millimeters also block the pore space of the material preventing a sufficient uptake of resins needed for the hardening of weakened zones in the material.

At Schloß Schwerin a gable with a square of nine 50x50x7 cm³ terracotta plates showing different portraits were investigated to detect the damages, finding the factors responsible for deterioration and to develop a suitable restoration concept for the plates. During the investi-

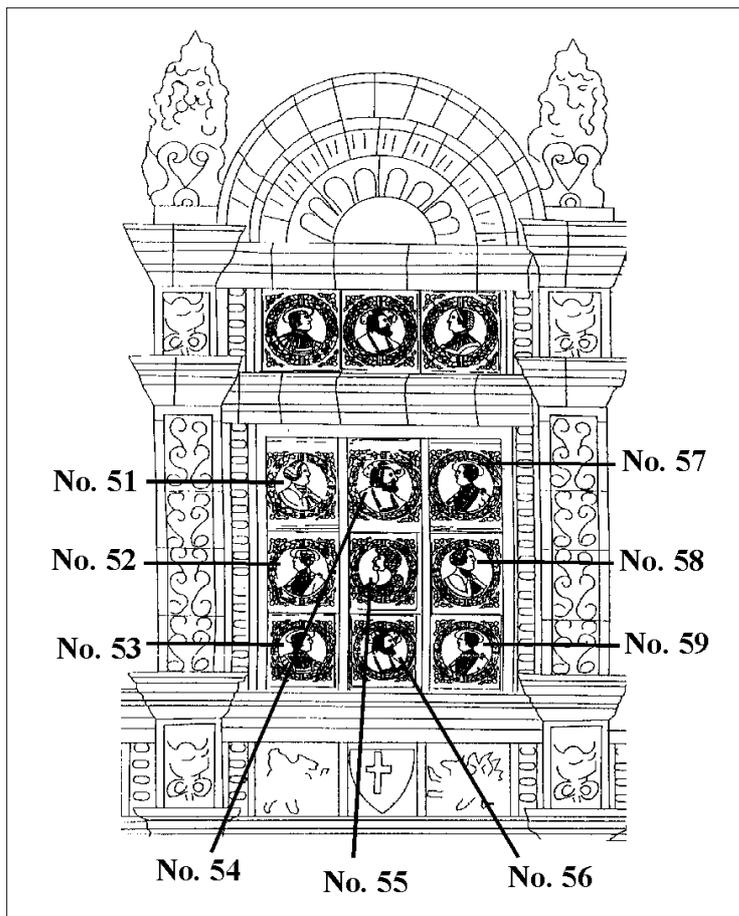


Fig. 1: Part of a gable at Schloß Schwerin with the used numeration of the terracotta plates.

gations lasting for more than one year the area was protected from the impact of rain. Figure 1 shows the gable at the "Neues Langes Haus" of Schloß Schwerin with the used numeration of the terracotta plates.

The deterioration phenomenon of the surfaces were mapped. For the application of stone consolidants information about weaken zones inside the material was also needed. To avoid deterioration during sampling procedures, the strength profile of the material was determined by means of the drill resistance technique. The speed of drilling a 3 mm hole with constant pressure and constant energy supply gives a measure of the material

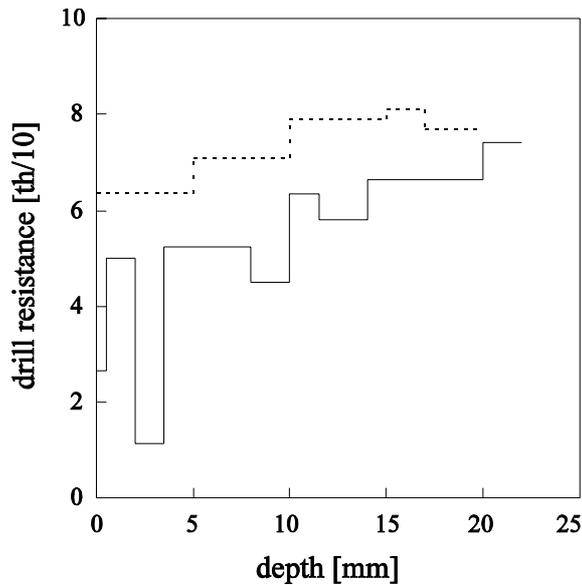


Fig. 2 Drill resistance at two points of terra-cotta relief no 56.

strength as a function of the depth. Using an empirical function which was developed in the laboratory for some 100 different stone material by correlation measurements, it is possible to estimate the flexural strength of a material with a precision of some ± 1 N/mm² (WENDLER and SATTLER, 1996).

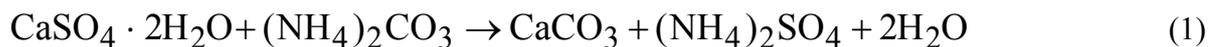
As demonstrated in figure 2, brittle zones with a dramatic loss of strength were found close to the surface of the terra-cotta plates. However, due to the enormous variations in material properties in the same relief, there are also areas showing a strength profile with only little weathering intensity.

Salt measurements showed concentrations of 3-10 weight percentages of gypsum mainly in the first millimeters of the surfaces. Lower concentrations of nitrates and chlorides in the plates were detected, which were, in comparison to gypsum, distributed homogeneously in the plates.

The capillary uptake acquired by Karsten tube measurements (WENDLER and SNETHLAGE, 1989) differed from plate to plate and even within different areas of the same plate. In some areas the uptake coefficient was far too low for a sufficient uptake of stone consolidants.

To prevent further damage and to open the pore space for strengthening resins two poultice techniques were tested for the gypsum contaminated terracotta plates. The first was carried out with a high volume of deionized water in order to dissolve gypsum blocking the pores important for capillary transport.

Furthermore, a treatment with ammonium carbonate solution was tested. This method was already used successfully for the treatment of gypsum contaminated wall paintings (MATTEINI and MOLES, 1983). In the initial step poultices with saturated ammonium carbonate solution are applied to the surface which transfers gypsum into calcite



and easy soluble ammonium sulphate according to (1). An excess of the reagents is irreversibly decomposed to ammonia and carbon dioxide.



Based on the method described by MATTEINI and MOLES a poultice with barium hydroxide is used afterwards in order to transfer ammonium sulphate into nearly insoluble barium sulphate and gaseous ammonia.



This treatment was not used on the terracotta plates because the precipitation of nearly insoluble compounds often resulted in an overstrengthening of the surface area which was not desired. Moreover, there is a risk that the reaction products calcium carbonate and barium sulphate are formed directly on the surface. A white residue would remain on the red coloured terracotta. In order to extract the excess of ammonium sulphate, a compress with deionized water was used as second step of the treatment. Coarsely grained quartz sand was added to the cellulose in order to achieve a gradient of humidity towards the outside, expecting that soluble salts would migrate along this gradient.

The efficiency of both desalination treatments was tested by measuring the salt content in different depths of the plates before and after the treatments as well as by the determination of the salt content in the poultices. Furthermore, the results were compared with the theoretically soluble amounts of gypsum in the porous material.

Karsten tube measurements for the capillary uptake and drillings resistance measurements for the detection of changes in hardness of the material were employed for an evaluation of the efficiency of the measures.

3 EXPERIMENTAL

For the detection of the initial state of the plates the salt content, the strength and the capillary uptake in different areas of the terracotta plates were measured.

For the determination of the salt content in different depths an improved sampling technique was used. Based on a commercial drilling machine a special device was added which allows to tune the sampling depth and to collect the drilling powder nearly quantitatively. With this technique the detection of all relevant soluble anions and cations within the powder from a drill of 6 mm in diameter and a depth of down to 5 mm is possible.

Samples for salt analysis were taken in the flat areas beside the portrait relief. If the state of weathering differed within one plate, samples were taken from both sides of the portrait.

The powder was dried at 30°C and extracted with deionized cold water. Poultices used for desalination were treated in the same way. For the determination of chloride, nitrate and sulphate ionchromatography was used, carbonate was detected by acidimetric titration. Sodium, potassium, magnesium and calcium were measured by atomic emission spectrometry. Ammonium was detected by colourmetric methods.

The capillary uptake was measured by Karsten tubes. Because of the structured surface of the plates special micro-tubes with a smaller active surface area were used (WENDLER, 1995). For the poultice application the surfaces of the plates were first wetted and covered with thin paper layers in order to guarantee a good adhesion to the terracotta material and an easy removal afterwards. For each 50 x 50 cm² terracotta relief 650 g of ARBOCELL PUR 200 cellulose material soaked with deionized water was applied. In order to achieve a sufficient solution of the gypsum in the surface of the plates during a period of one week 9 liter of water per plate were given to the compresses. To prevent evaporation the surfaces of the poultices were covered with PE-films for this time.

After one week the cellulose used for wetting the material were removed and compresses aiming at the extraction of the salt were applied. For this purpose quartz sand and glass spheres with a diameter of 400 to 600 µm were added to the cellulose material. The poultices were soaked with water and dried out on the surface of the relief afterwards. From both measures 10x10 cm² areas of the poultice material were taken for the determination of the salt content.

For the application of ammonium carbonate, cellulose compresses with saturated (NH₄)₂CO₃-solution were applied for 18 hours on plate no 53, 55, 56 and 57. Afterwards a mixture of cellulose and quartz powder was also applied allowing to dry on the surfaces of the terracotta plates. The gradient of moisture should transport the ammonium sulphate towards the surface of the relief into the poultice.

4 RESULTS AND DISCUSSION

The maximum of gypsum (CaSO₄•2H₂O) content is always found in first millimeters of the relief and decreases exponentially to background concentration within the first centimeters. Other ions were found in much lower quantities.

The gypsum content is most probably a result of dry deposition of SO₂ emitted from the heating systems of the castle as shown by an estimation of deposition rates. Nitrates and chlorides were found in much lower absolute concentrations but in very similar ratios to each other, indicating that rain water intrusion from the back side of the gable is responsible for the enrichment of both ions (WITTENBURG, 1995).

4.1) MEASUREMENT OF THE WATER UPTAKE

Figure 3 shows the water absorption coefficients w calculated from Karsten tube measurements for the untreated material in comparison to those received after the two different compress applications.

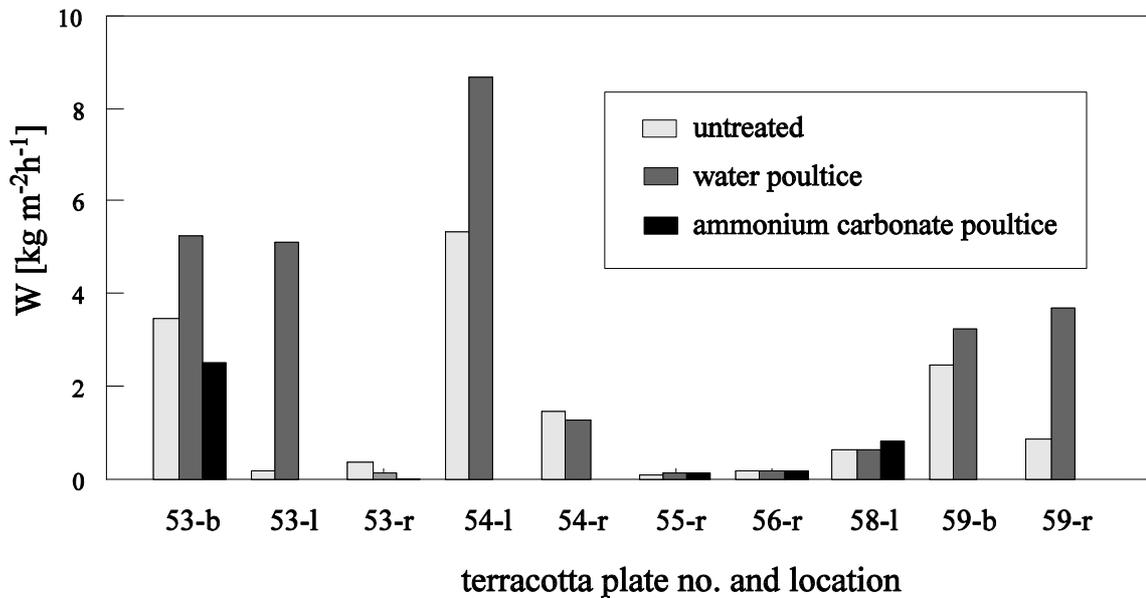


Fig. 3 Water absorption coefficient (W) for different areas of the plates in the untreated state and after the two desalination treatments.

As already mentioned, the ammonium carbonate method was merely applied at the relief 53, 55, 56 and 58 as a subsequent step after the application of the water poultice. It can be recognised that the application of the water poultice lead to an enhancement of the water absorption in some 50 % of all cases. However, the relief 55 and 56 which show a very low water absorption in the initial state due to a very dense sintered surface did not show any increase after poultice application. In these cases, the limited absorbency of the material is a consequence of the material properties and presumably not caused by the presence of gypsum in the surface zone.

In contrast, the ammonium carbonate compresses did not lead to an increased water absorption except a negligible enhancement in the case of relief 58.

4.2) SALT CONTENT AFTER WATER POULTICE TREATMENT

For an evaluation of the desalination efficiency the sulphate contents found in the relief and in the compresses were transferred to square related values. For this calculation the measured density of 1,8 g/cm³ and the sulphate concentration of the first 15 mm of the terracotta relief were considered.

In figure 4 the area related sulphate content in the terracotta plates before and after the poultice treatment with deionized water are given.

Some plates show a reduction of the sulphate content while others even display higher concentrations. No clear tendency could be observed as the variation in the material seems to be of high influence.

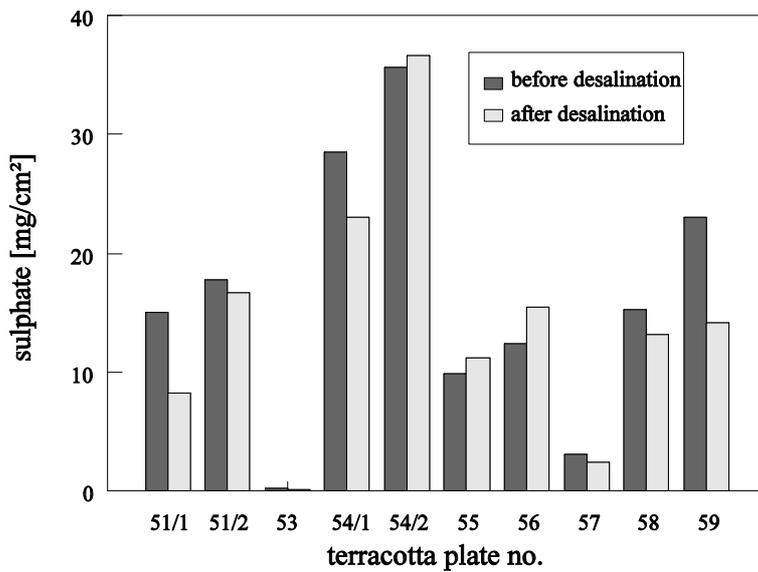


Fig. 4: Sulphate content before and after the desalination treatment with deionized water.

order to compare the theoretically soluble sulphate content which should be found in the poultices if the water accessible porespace (27 vol. %) of the first 1,5 cm of each plate would be filled with water and exits with saturated gypsum solution (1,97 g/l) is plotted. Results from relief no 57, 58 and 59 are close to this value. On plate no 57 the gypsum content in the terracotta was comparably low. Even for this plate a reduction of merely 19,4 percent was reached.

The poultices used for wetting the surfaces showed even lower salt concentrations and were not considered for this calculation.

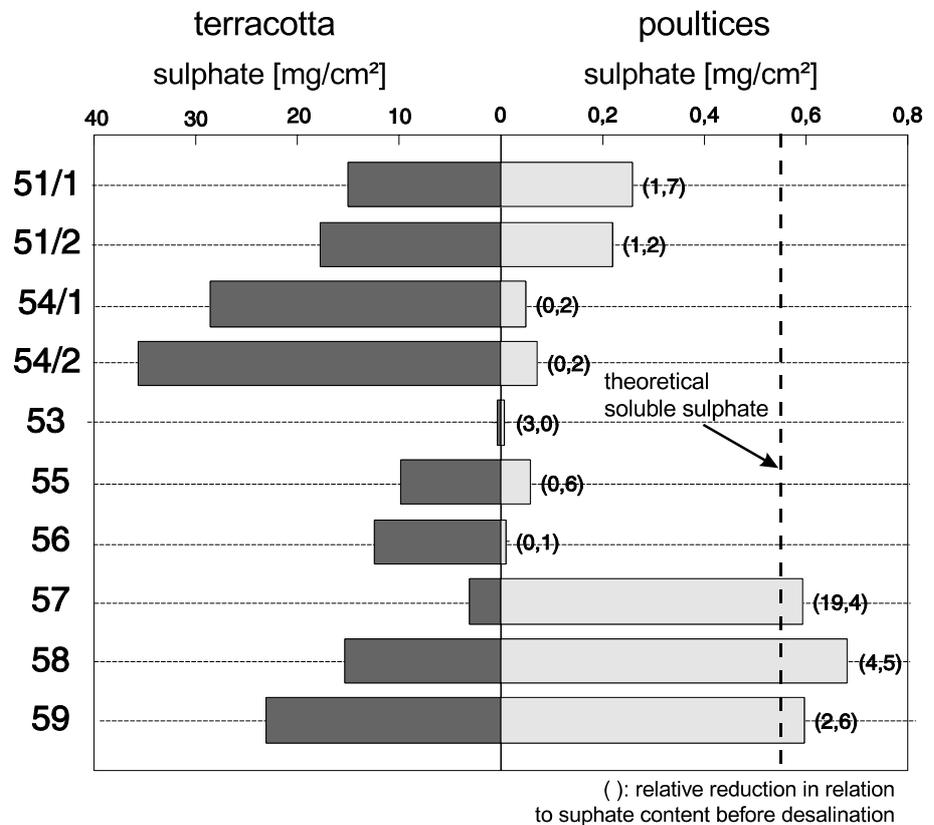


Fig. 5: Sulphate content in the terracotta plates and in the poultices, the relative reduction in relation to sulphate content before desalination.

For a validation of the sulphate reduction in figure 5 the results from the analysis of the poultice material are given.

As the results of the salt analysis of the terracotta material before and after the treatment already indicated, the reduction of the sulphate content in general was low. Most of the poultices reduced the sulphate content of the plates only for values in the lower percentage range. In

4.3) SALT CONTENT AFTER AMMONIUM CARBONATE TREATMENT

For an evaluation of the efficiency of the treatment with ammonium carbonate solution aiming at the transformation of gypsum, the ion content of the poultices as well as the salt concentration in the terracotta plates were considered.

The analysis of the area related sulphate content of the compresses allowed the calculation of the efficiency of this measure. The relative sulphate reduction in relation to the content after the water poultice treatment is given in table 1.

Tab. 1: Area related sulphate content (SO_4^{2-} -con.) calculated from ammonium carbonate (Am) and desalination poultices (D) and relative SO_4^{2-} -reduction.

sample-no.	SO_4^{2-} -con. poultice [mg/cm ²]	relative SO_4^{2-} -red. [%]	sample -no.	SO_4^{2-} -con. poultice [mg/cm ²]	relative SO_4^{2-} -red. [%]
53 Am	0,0034	2,2	53 D	0,0193	12,3
55 Am	0,0432	0,4	55 D	0,2115	1,9
56 Am	0,0154	0,1	56 D	0,0431	0,3
58 Am	0,0422	0,3	58 D	0,9725	7,4

As for the pure water application higher concentrations were found in the desalination poultices. The efficiency was little higher than that of water poultice treatment. The highest relative value was found for plate no 53 (12,3%). This is due to the fact that the absolute sulphate content of this plate was very low (see fig. 4).

An evaluation of sulphate reduction by comparing the SO_4^{2-} -content analysed in the drilling powder before and after the treatment was not possible. The reduction was too low in relation to the deviation of the absolute content in the terracotta plates. Changes in the relative contribution of single soluble ions will nevertheless yield information about the reaction that occurred in the plates.

In figure 5 the anion and cation content found in plate no 56 after ammonium carbonate treatment is plotted. Ammonium was found in high concentrations especially in the first 5 mm of the plate indicating that the reaction between gypsum and ammonium carbonate was quite successful. Carbonate did not contribute to the soluble ions in considerable amounts which implies that the reaction to calcite was obviously nearly quantitative.

On two of the four plates treated with ammonium carbonate (no 56 and 58) the transformation was much lower and the anion and cation content indicated that still most of the gypsum was

present. The corresponding cation to ammonium still was soluble carbonate as can be seen in figure 6.

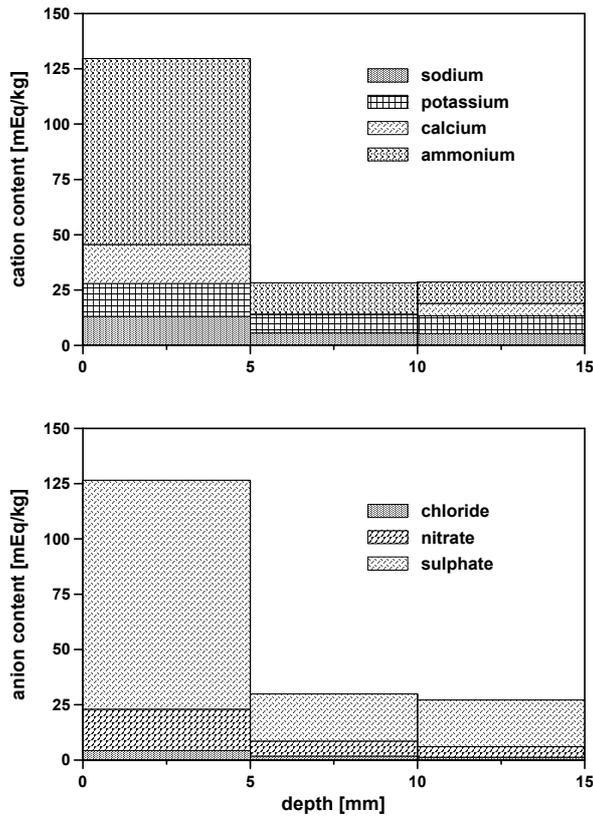


Fig. 6 Ion content of plate no. 56 after treatment with ammonium carbonate solution.

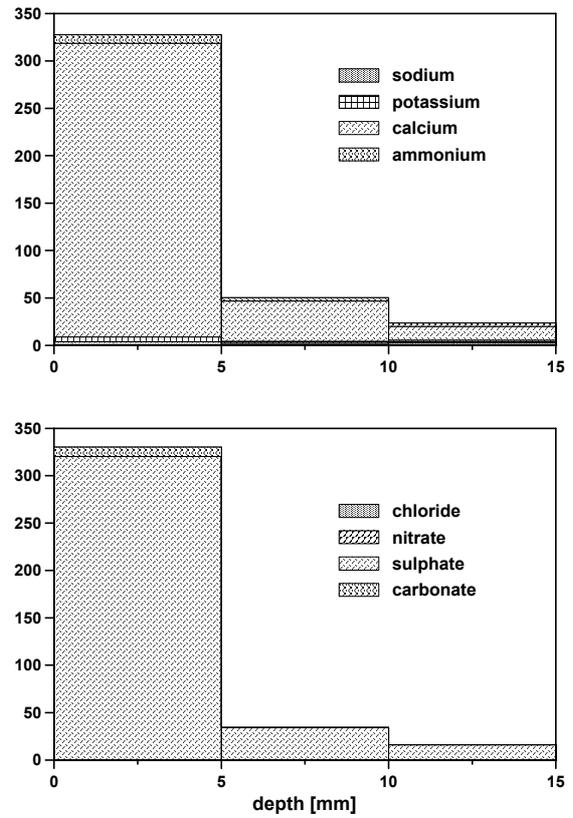


Fig. 7 Content of plate no. 58 after treatment with ammonium carbonate solution.

The efficiency of this treatment differed very much. The porosity and the possibility for a sufficient uptake is very dependent on the conditions of the single plate.

5 CONCLUSION

Treatment with water soaked compresses for the reduction of the gypsum content of terracotta resulted only in a minimal wash-out of the calcium sulphate. In spite of the high volumes of water used for the treatment, the low solubility of gypsum is the limiting factor for desalination of the relief.

Also after the treatment with ammonium carbonate only small amounts of sulphate extracted by the second, water soaked compress were measured. Nevertheless, the transformation of gypsum into ammonium carbonate within the porespace of the terracotta was quite successful for some of the plates. If the soluble ammonium sulphate will remain in the upper layer of the terracotta crystallisation cycles can be expected when the relative humidity of the surrounding

atmosphere reaches values beyond or below 80 %. This might even lead to an enhancement of weathering after the treatment. The extraction of the reaction products from the terracotta is one of the main problems of the whole procedure.

The water uptake coefficient measured by Karsten tubes increased after the water poultice treatment for most of the plates under investigation. In spite of the low desalination efficiency it can be assumed that the capillary active pores were to some degree affected by this measure.

For further applications a longer duration of ammonium carbonate compresses on the surfaces combined with a better extraction would be desirable.

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