EXTRACTION OF SALTS ON MONUMENTS - EVALUATION OF RESULTS FROM APPLICATIONS AND BOUNDARY CONDITIONS

SALZEXTRAKTIONEN AN BAUDENKMÄLERN - BEISPIELE AUS DER PRAXIS UND RANDBEDINGUNGEN

EXTRACTIONS DE SELS SUR DES MONUMENTS HISTORIQUE - PRESENTATION D'APPLICATIONS PRATIQUES ET PRISE EN CONSIDERATION DES CONDITIONS LIMITES

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Summary

The extraction of salts on some monuments by using cellulose - compresses and compress - plasters consisting of lime mortar are introduced. The degree of desalination was up to 90% regarding nitrates and chlorides, while less soluble sulfates (e.g. gypsum) showed less success. The results are compared to the state of the art. The boundary conditions of these methods and the physico - chemical mechanisms are discussed.

Zusammenfassung

Es werden Entsalzungsversuche von Versalzungsbereichen an mehreren Bauwerken vorgestellt. Hierbei kamen Zellulosekompressen und Kompressenputze zum Einsatz. Der Entsalzungsgrad betrug bei Nitraten und Chloriden bis zu 90% und war bei beiden Verfahren vergleichbar gut, wohingegen schwer lösliche Sulfate (z.B. Gips) Probleme bereiten. Die Ergebnisse wurden dem Kenntnisstand gegenüber gestellt und mit theoretischen Überlegungen zu den physiko - chemischen Wirkungsmechanismen und Reaktionsbedingungen verglichen.

Résumé

Des examples de déssalage d'efflorescence sur plusieurs bâtiments sont décrits. A cet effet on utilise des compresses de cellulose et enduits à compresse. Le degré de déssalage pour nitrates et chlorides allait jusqu'à 90% et etait bon pour les deux procédés tandis que les sulfates difficielment solubles posent des problèmes. Les résultats ont été comparés avec d'autres méthodes de déssalage et les réflexions théoretiques sur les effets physico-chimiques et les conditions limite ont été faites.

Key-words:
monuments, salt, desalination, cellulose - compresses, compress - plasters, nitrates, chlorides, sulfates, diffusion

1 Introduction

Very often monuments can be observed showing zones of efflorescences and remarkable contents of salts.
Both effects the decay of stone, because of the crystallization pressure and the chemical attack [7; 12].
For the conservation and restauration of precious monuments a non destructive method of desalination (salt extraction) is urgently needed. This article presents some cases of desalination by different methods and discusses the results.

2 The origin and the appearance of efflorescences

There are multiple reasons for a salt content e.g. solution of minerals, rising damp, salt movement from mortars and of course air pollution deposing mainly SO_2, NO_x, CO_2, dust etc. Regarding the appearance at the monument three cases are the most common ones:
Zones of rising damp from the ground, hygroscopic stains resulting from solutions which prevent the drying processes (see fig. 1) and deposition of pollutants on the surface forming salts or black crusts (fig. 2).
Depending on the relative humidity and the solubility all salts form either efflorescences on, or brines within the stone material.

Fig. 1: A typical zone of rising damp, damaging the plaster and stone below and forming white efflorescences.

Fig. 2: Mask of a gothic frieze showing severe damage by salt crystallization like delaminations and salt crusts.

3 State of the art of desalination methods

[11] gave a survey of references and tested three methods by experiment: water bath, compress methods and electro-chemical desalination. For these experiments NaCl, KNO_3 and $MgSO_4$ salts were used to contaminate sandstones. Hence the most relevant results are:

1. The water bath proved to be the most efficent method to remove salts, but the negativ effects are corrosion of some stones and it can only be applied on removable objects.
2. With all three methods KNO_3 and NaCl are the easiest salt species to remove.
3. The efficiency of the compress method is less than the water bath.
4. When treated once the electro - chemical method just showed an effect of 15 - 30%.

In general [11] concluded that there is no desalination method for all cases but the selection of the method has to be adapted to the salts present and the stone material.

3.1 Details of the compress methods

The compresses have to cover completely the walls containing salts. The layers should be of a constant thickness of at least 2 centimeters.
Basically there are several materials suitable for extraction purposes:

1. cellulose pads or flakes,
2. clay minerals, especially expandable clay minerals ([11] suggest fillers containing attapulgit),
3. compress plasters (plastic mortars containing no chemically problematic ingredients) where a slow enrichment of salts can take place before they are removed.

Regarding the application of the clay or cellulose compresses there are two methods which could be used:

1. Application of thin layers, which are quickly dry (a few hours) and then taken off [11,4].
2. Controlled wetting of the salt containing parts, keeping the compresses wet to keep up diffusion. Then they are removed in a wet condition.

4 Results of salt extractions on monuments

4.1 Salt extractions using cellulose compresses

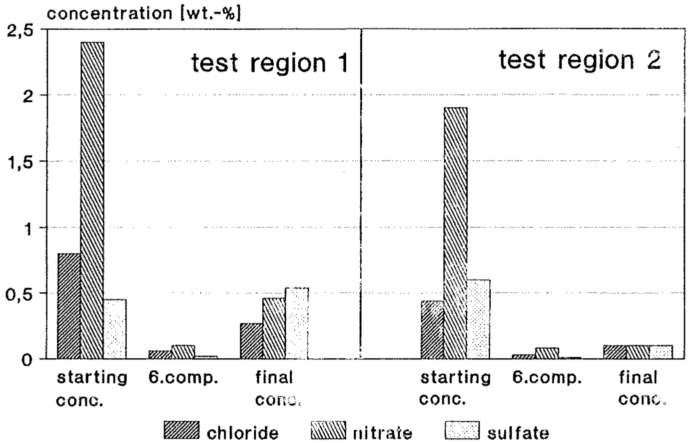
This article presents examples of the latter method and for compress materials cellulose flakes (Arbocel) and very rich lime mortars were used.
The applications lasted at least 5 days. Before the extraction the soluable salt content of the walls was analyzed by ion chromatography and the efflorescences by XRD.

In some cases the treatment had to be repeated several times. After each application the salt content of the compresses was controlled to decide the next step and to define the degree of extraction.

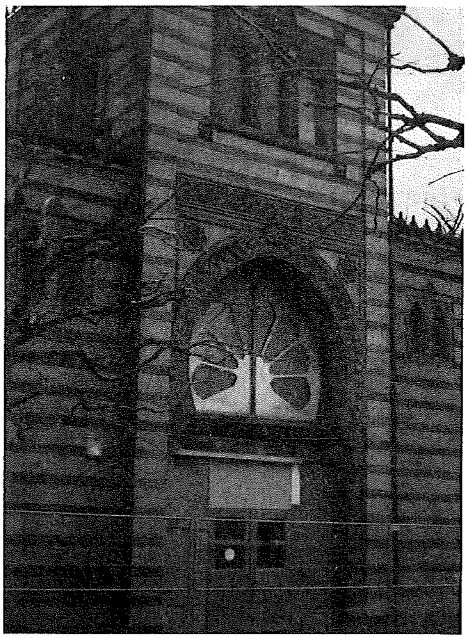
The Gothic church St. Paul / Eßlingen was built from local Stubensandstone. After cleaning it showed hygroscopic zones coming from formerly existing rising damp. In addition there has been a large uptake of thawing salts (NaCl). Further salts identified were gypsum and Na_2SO_4 and in the pore waters Na, K, NO_3, SO_4 and Cl were found.
Six extraction phases were performed on a test area near the west portal.
The analyses showed that each extraction removed about 15% of the salts (fig. 3). Compared to the original values 65 -90% of the chloride and nitrate salts were removed (table 1).
The sulfate content was just lowered by about 10%. Probably the reason is the lesser solubility and diffusion from neighbouring parts.
At the end the results may be called satisfying because of the disappearence of the hygroscopic stains and efflorescences.

Table 1: St. Paul / Eßlingen, results of salt extraction, using cellulose compresses (in wt.-%)

Sample	Description	Cl^-	NO_3^-	SO_4^{2-}
1	stone, untreated	0.80	2.4	0.45
2	6. compress	0.06	0.10	0.02
3	stone after the 6. treatment	0.27	0.46	0.54
access of extraction		66.3%	80.8%	-20%
4	stone, untreated	0.44	1.9	0.6
5	1. compress	0.03	0.08	<0.01
6	stone after the 6. treatment	<0.1	<0.1	0.54
access of extraction		77.3%	94.7%	10%



<u>Fig. 3:</u> St. Paul / Eßlingen, results of salt extraction (6x), cellulose compresses.



<u>Fig. 4</u>: View of the outside of the Damascener Hall (moorish style) during the renovation period. The socle reveals stains because of salts with hygroscopic effects.

Another monument revealing hygroscopic stains, discolourings and high nitrate contents is the Damascener Hall, built in 1890 which belongs to the Stuttgart zoo "Wilhelma" (fig. 4).
Inside this building the wall covering is made of precious red to yellow stucco marbles. In this case plaster extractions as well as cellulose compresses were applied.
The comparison of the analyses shows (table 2) that at least 50% of the nitrate was removed and that in general the first extraction was the most successful.

Table 2: Damascener Hall, Stuttgart, factors of extraction for the application of cellulose compresses.

Sample		factors of extraction	
		extraction 1	extraction 2
A 4	chloride	4x	5x
	nitrate	3x	2x
B 8a	chloride	0,5	0,02
	nitrate	0,8	0,005
C 10	chloride	0,8	0,2
	nitrate	0,7	0,1
D 13	chloride	0,5	0,3
	nitrate	0,5	0,14

4.2 Salt extractions using lime plasters

In the Damascener Hall plaster compresses could be applied on stone and brickwalls for 1.5 years during a period of reconstruction (fig. 5).

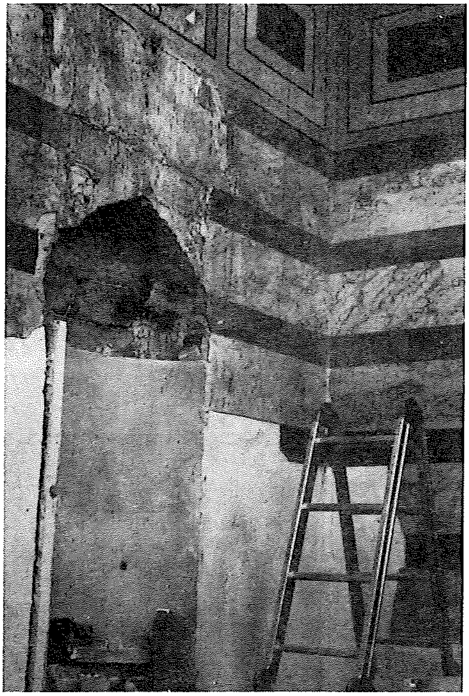


Fig. 5: The application of compress plasters on the walls inside the building. These plasters are expected to accumulate the salts from the masonry behind and later on be removed.

Different recipies of mortars could be tested. The mortars were pure lime mortars and mortars containing low amounts of various cements. The pure lime mortars revealed the best results (table 3, fig. 6, 7, 8).

Table 3: Damascener Hall, Stuttgart. Factors of extraction for desalination using lime plasters.

Sample	starting concentration (wt%)			Factors of extraction** durch die Putze (wt%)		
	chloride	nitrate	sulfate	chloride	nitrate	sulfate
A 4	0.39	0.22	0.01	1/3	1/4	2.5
C 9	0.02	0.01	0.71	1/2	1	1/70
C 10	0.08	0.17	1.61	1/7	1/5	1/25
D 13	0.07	0.25	*46.65	7/10	1/2	---
A 2	0.01	0.03	0.26	3.6	4/5	1/10
A 3	0.03	0.14	1.22	1/2	1/5	1/30
B 8a	0.64	1.96	*43.40	1/4	1/7	---

* old stucco marble, containing gypsum

** removed contents

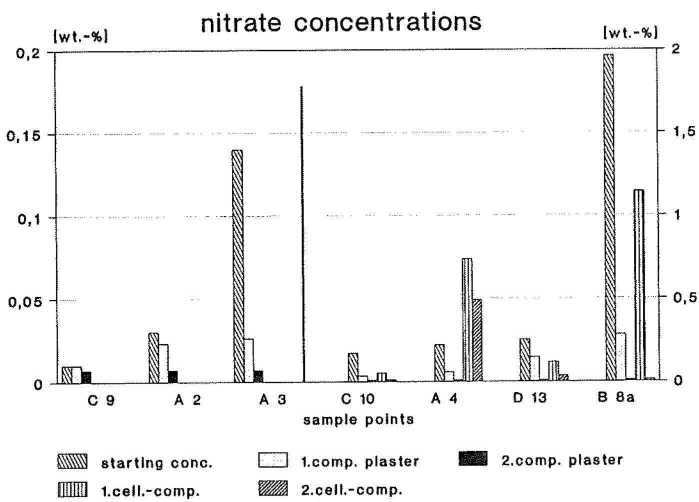


Fig. 6: Nitrate concentrations in cellulose compresses and compress plasters in comparison to the untreated stone, Damascener Hall, Stuttgart.

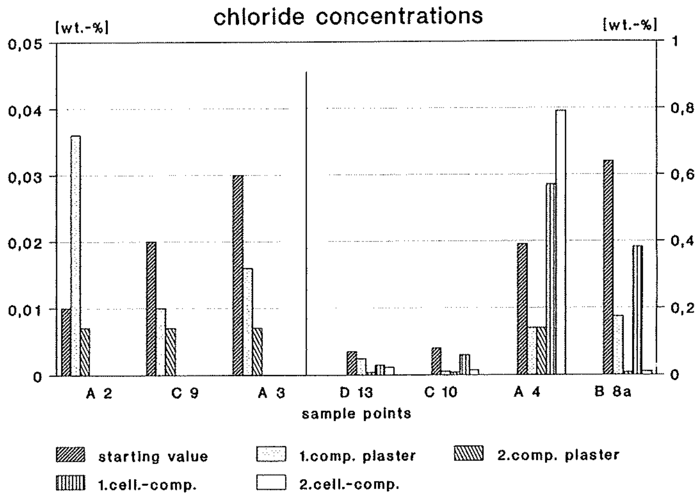


Fig. 7: Chloride concentrations in cellulose compresses and compress plasters in comparison to the untreated stone, Damascener Hall, Stuttgart.

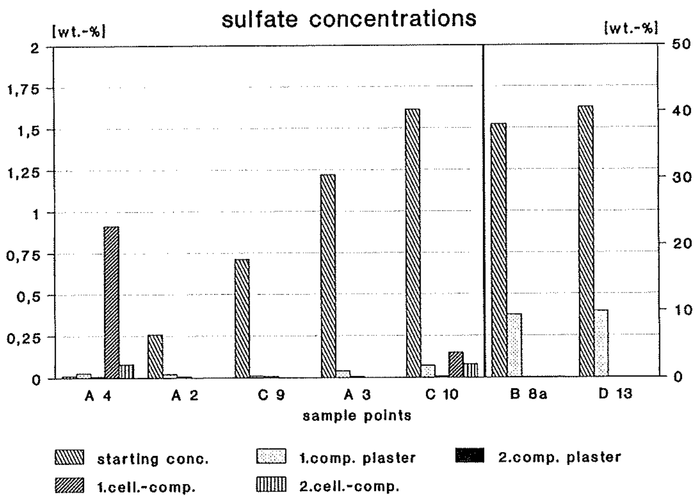


Fig. 8: Sulfate concentrations in cellulose compresses and compress plasters in comparison to the untreated stone, Damascener Hall, Stuttgart.

4.3 Disturbances because of application mistakes

Additionally to the physico-chemical factors disturbances resulting from wrong applications, listed below, may occur:

1. The water content of the stone was not high enough to allow diffusion processes.
2. The compresses didn't contact the wall everywhere, the ion diffusion is therefore interrupted.
3. In our opinion a very fast drying process may cause backward diffusion because of withdrawal of capillary seams or the diffusion is slower than the drying process.

5 Physico - chemical effects and boundary conditions

Apart from the effects mentioned by [11]: solution processes, partly competing reactions, and the role of the reaction typ of the dissolution, further effects should be considered.

1. The main (ion-) mass transport proceeds via diffusion therefore the diffusion should be discussed in detail.
   The diffusion velocity is strongly dependent on the pH - values and the amount of short term adsorption and desorption on active surface sites.
   [3] proved that the chloride diffusion in concrete shows diffusion coefficients (D) ranging from $D = 10^{-7} - 10^{-9}$ (cm^2/s) in alkaline solutions to $D = 8*10^{-6}$ in neutral solutions.
   Investigating sandstones from Baden Württemberg [6] measured diffusion coefficients for NaCl and $CaCl_2$ solutions ranging from $D = 2.1*10^{-5}$ up to $9.8*10^{-8}$ (cm^2/s).
   Using these values for calculating the Fick law of diffusion the velocity of ion movements are in the range of about 3-7 days for 2 centimeters (a normal range for high salt content).

2. The ionic mass transfer taking place during this process (Q/t) was also investigated by [6]. The mass transfer is about 0.15 to 9.0 $mg/ld^{-1}cm^{-2}$. These values should be used to calculate the period of desalination.
3. A small amount of salts can not be removed because of adsorption on porewalls or double layer effects.
   The adsorption depends on the number and potential of surface sites and the amount of internal surface.
   Basically Al - containing minerals, especially clay minerals have very reactive surfaces, while silicates show less absorption.
   [9] measured the adsorption uptake of phosphate on halloysite, allophane and imogolite to be 950 ppm - 1.9 wt%.
   The sulphate adsorption on kaolinite can increase up to 0.25 wt% [8].
   Like expected quartz adsorbs only about 0.07 wt% chloride [5]. Regarding the very reactive gases CO and NO quartz surfaces adsorbed up to 0.22 wt% [2].
   In addition [10] found, that during weathering ion exchange takes place and therefore a part of the salts is fixed to clay minerals while other ions are released.

Therefore, depending on the mineral content of the stone, a remarkable amount of salts is bound to the internal surfaces and will stay in the pore space.

6 Conclusions

Using cellulose compresses or mortar compresses on monuments a high extent of salt extraction may be achieved. The degree of extraction is not as good as in laboratories but this is caused by irregular salt distributions and ion movements from neighbouring parts.
The treatment with wet layers seems to work almost as well as the drying methods, further investigations should be done on this subject.

Knowing the physico - chemical effects, the ions in solutions, diffusion velocities of each ion, mass transfer by diffusion, permeability of the stone (which can partly be found in references or may be measured separatly), etc. a theoretical calculation of desalination time and amount of extraction could be done.
A brief calculatory comparison of the experimental data obtained from the extraction on the monuments to the theoretical data showed a good agreement.

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7 Literature

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