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Desalting a wall painting after application of silicic acid ester

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1. Introduction

Wall paintings with extremely high salt contents often only survive in a rather disastrous state, so that they are in danger to be given up. Our presentation describes the approach to the treatment of such highly problematic wall paintings, situated in the crypt of St. Maria im Kapitol. It was the aim to find a consolidating method, that did allow to desalinate afterwards.

To find an appropriate consolidant we first formulated a list of requirements. After preliminary tests that gave some ideas about the behaviour of different products towards salts, we selected three products to be tested more completely in the laboratory. The consolidant which had shown the best laboratory performance was then applied to a test area in St. Maria im Kapitol and the possibility to desalinate afterwards was examined.

2. The wall paintings at the crypt of St. Maria im Kapitol

The church of St. Maria im Kapitol, in Cologne, Germany, is regarded as one of the most famous Romanesque fabrics of the 11th century. Five side chapels in the crypt bear the remnants of 12th century mural paintings.

The crypt suffers from very serious salt problems, because its walls are penetrated by ground moisture; the crypt was used as a salt store in the 19th century; the vaults were repaired using concrete; during World War II the whole church was seriously damaged by bombs and consequently exposed to weather for several years; finally during the 1960's the wall paintings were treated with water glass. Cyclic crystallisation of salts as described by Laue (in press) was the result of this devastating history.

The work we present here focused on a painting in the vault of the north-eastern side chapel of the crypt. The painting is executed on a brownish lime render with a thick whitewash layer on top. Analysis of the whitewash layer showed that it contained a very high amount of gypsum, which, how we suppose, must have been added originally.

The condition of the original paintings and their supporting render today is very poor, so that any touching results in the risk of losing more original material. Although the paintings were monitored over more than a year, salt efflorescence was never observed. The quantity of losses of surface material in this vault, which were collected and weighed regularly, correlated perfectly with the room climate and the cyclic salt crystallization at the lower parts of the walls, where crystallization occurs only during dry winter period. By this it could be shown, that the main deterioration factor is actually the activity of the salts, so that a reduction of the salt content in the renders would most certainly ease the situation.

The only promising method to desalinate these wall paintings and their supporting renders seemed to be to apply compresses, however the renders and the paint layers were so fragile that they could not be touched, and hence desalinated, without being consolidated first.

The only example of wall paintings that were treated in a similar way, was published by Hammer (1987/88). Therefore we felt that it was necessary to test the consolidants in the laboratory before applying them to the original wall paintings.

3. Selection of consolidants for the laboratory tests

Our investigations on the wall paintings in St. Maria im Kapitol led to the formulation of the following list of requirements for the consolidant and its method of application:

The application method for the consolidant should cause as little physical stress to the paintings surface as possible, this point will be further discussed below (see 6. 1).

The consolidant should:

=> easily penetrate the porous structure of the mortar
=> not alter the paintings appearance not seal the
=> surface against water vapor
=> not be hydrophobic after treatment not affect a desalination after
=> the consolidation not be easily affected by micro-organisms its
=> consolidating effect should not be strongly influenced by salts.

Silicic acid esters (SAE) which are meanwhile used for some decades as stone consolidants, seemed to fulfill the majority of the above listed requirements. However there is only very little known about the behaviour of SAE in structures that are contaminated by salts.

The scarce literature about this problem offers somewhat contradictory information, e.g. Sattler (1992) claims that salts strongly affect the hardening of SAE, whereas from the restoration of ceramic archaeological objects, it is known that the use of SAE does not hinder later desalination (Sander-Conwell, 1995), which implies that SAE must have had a consolidating effect in spite of the presence of salts.

Grassegger (1990) describes that SAE gels formed under the presence of salts have higher content of adsorbed water and show less silanol content than salt free gels, which might have a diminishing effect on the stability of the gels.

To better understand the reactions which might occur between silicic acid ethyl esters and salts we mixed in a preliminary test different rather frequently used SAE products with salt mixtures (sodium nitrate, sodium chloride and gypsum), with salt free and salt contaminated lime mortar particles and with salt contaminated particles, that had fallen of the wall paintings at St. Maria im Kapitol. The hardening of these samples was observed and the products compared amongst each other, by estimating their speed of reaction, their influence to the sample colour and their tendency to crack. It could be seen that the time for consolidating became much longer in the presence of salt compared to salt free samples.

From these experiments three silicic acid ethyl esters were selected to undergo an extended laboratory test. Funcosil-OH (OH stands for "without hydrophobic effect"); Funcosil 300 (a solvent free SAE); Motema 28 (an uncatalized SAE) was used in a 5:1 mixture (by volume) with Funcosil OH. All three consolidants are frequently used by restorers in Germany.

4. Sample preparation and laboratory test methods

The laboratory samples should match as perfectly as possible the state and the salt content of the mortars on site, because the main aim of the work was to find out which consolidant did fit best to the requirements at St. Maria im Kapitol, as listed above.

Previous experiments had shown, that lime mortars even when prepared with very little binder did still show too much cohesion and that it was difficult to cure the mortar so that it did not contain any uncarbonized lime. Therefore it was decided to use a lost mixture of sand and calcite ($CaCO_3$). The quartz sand was sieved to have the same grain size distribution as the original mortars and it was made sure that the ratio of sand to calcite was the same as in the original.

The salt mixture was calculated from an average of twelve samples all taken in the vault which should later be treated, to make sure the final composition of the samples did match as closely as possible the salt contaminated renders (A in table 1). Gypsum was added to the samples as a powder. The other salts were added as a solution. The final mixtures were then thoroughly mixed and filled about 2 cm deep into rectangle glass basins (16 x 8cm) and left to dry to constant mass in a climate of about 50-70 % relative humidity and 23° C.

The samples contained about 3 % of water free salt (IS in table I; description of the method of the quantitative salt analysis see appendix). From weight loss after the water extraction we know however, that this corresponds to about 5 % total salt content (crystal water of the salts), therefore this group of samples will further be called the 5 %-group. A second group of samples was prepared analogously to contain about 10 % salts (D in table 1), to see what effect an even greater salt content would have to the consolidants and the possibility of desalting. One salt free sample was prepared to serve as a blank. The complete list of samples with their amount of salt and type of consolidant is given in table 2.

	Na^+	**K^+**	**Ca^{++}**	**Mg^{++}**	**Cl^-**	**NO_3^-**	**SO_4^{--}**	**IB**	**IS**
A	64	17	127	33	107	185	42	25	27301
B	70	20	121	36	109	201	46	0	28848
C	65	<20	176	42	127	207	32	102	30032
D	176	49	273	95	323	506	29	73	64820

Table 1

A = Average salt content measured the original mortars;
B = salt mixture added to the laboratory samples of the
5 %-group (calculated values);
C = amount of salt actually measured by water extraction in the laboratory
samples of the 5 %-group
D = salts measured in the 10 %-group.
(IB = ionic balance; IS = sum of measured ions).
All values[µmol/g sample] except for IS, which is given in[µmol/g sample].

sample name	salt content	consolidant
lb	none	Funcosil-OH
3a	5	none
3b	10	none
4a	5	Funcosil-OH
4b	10	Funcosil-OH
5a	5	Funcosil 300
5b	10	Funcosil 300
6a	5	Motema 28: Funcosil-OH = 5:1 (by volume)
6b	10	Motema 28: Funcosil-OH = 5:1 (by volume)

Table 2 -*List of laboratory samples, with their salt content and type of cosolidant.*

From table 1 it can be seen, that, with the exception of calcium, the concentrations of the ions in the laboratory samples (group C) are very close to the ones measured as an average in the original plasters (group A), The high calcium content is probably due to a better solubility of the calcite added to the laboratory samples, than of the calcite of the original render. This might also be the reason for the elevated ionic balance (IB) of sample C.

In spite of the high salt concentrations, there were no salts observed to crystallize on the 5 %-samples and only some traces of little salt crusts could be seen on the 10 % samples. Only when examining the 5 % samples with the secondary electron microscope some sodium nitrate and chloride could be found.

The consolidation of the original wall paintings with SAE was done by capillary imbibition (see below 6.1). This method however was not applicable to our laboratory samples, which consisted of loose sand and hence could only be treated from above. Therefore we calculated the amount of SAE which was necessary to wet the sample material to a similar extent as the imbibition method would do, and poured the adequate volume (1,2 g of SAE per 10g sand) on the samples. In order to have a homogeneous distribution of SAE, the material was stirred thoroughly and afterwards the surface was flattened without executing pressure, to avoid any sedimentation or segregation of material.

5. Results

5.1. Observation during curing of the samples

After the addition of the SAE the samples were left to cure in a climate of about 50-70 % relative humidity and 23° C. For over three month they were regularly examined for alterations in color, hydrophobic behaviour, smell, hardness and weight change.

Colour: some SAE do change the colour of a treated surface. Both Funcosil 300 and the mixture of Motema 28/Funcosil OH did result in hardly any colour change of the samples, when compared to untreated samples.

Weight change: during the hardening reaction SAE loses weight because the solvents and/or parts of the SAE evaporate. Therefore the weight change gives an indication of the amount of reacted SAE which remains in the material, and this gives an indication on the time of reaction of the SAE (figure 1). However, for several reasons the samples were not kept in a completely constant climate during curing, so that the presence of hygroscopic salts did also result in weight changes (curves 3a and 3b in figure 1)

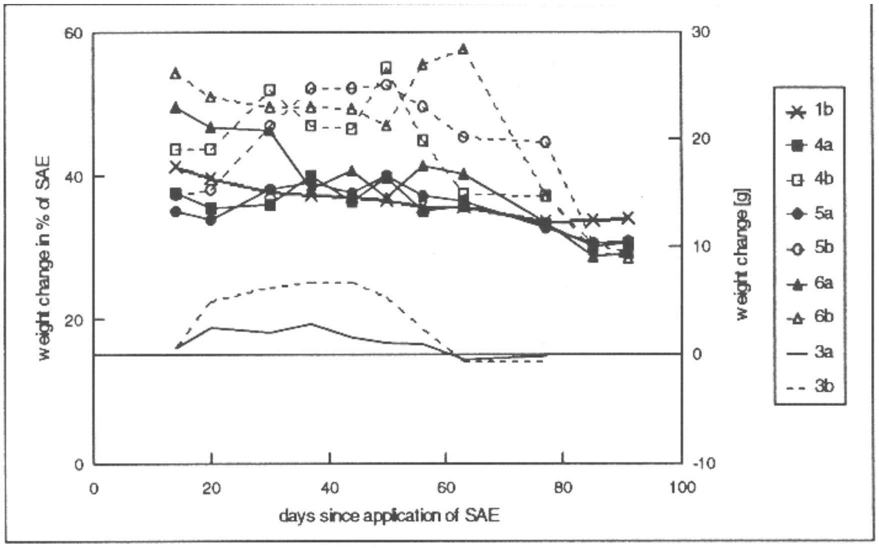


Fig. 1 - *Weight change in % of SAE during the hardening reaction of the consolidant, and absolute weight change in g of the two samples 3a and 3b, containing no SAE.*

From figure 1 it can be seen, that the samples containing 10 % of salt changed their weight much more irregularly than the samples containing 5 % of salt. Further it can be seen, that the samples consolidated with the Motema, 28 and Funcosil-OH mixture (6a and 6b) reduced their weight less continuously than the samples treated with the other two products.

Hardness: the hardness was tested by what we called the "needle test". A needle of about 5 grams of weight was falling from a distance of 5 cm on the surface of the sample. As long as the sample is still soft the needle will penetrate and stick, whereas on a hard surface the needle will bounce off. In each go this was repeated about ten times and it was counted how many times the needle did either stick or bounce off.

The amount of times that the needle did bounce off divided by the number of repetitions was calculated and called "B". If B equals one, this means, that the needle did always bounce off and therefore, that the sample was hard; whereas a low value for B meant, that the sample was (still) soft

In this "needle test" all samples containing 10 % salt (curves with open symbols in figure 2) did remain rather soft. Funcosil 300 did show the best performance regarding hardness, which can be seen by its B value remaining close to 1 after only a few days of curing time.

5.2. Salt analyses of desalting compresses of the laboratory samples

After curing the samples for over three months desalting compresses of Arbocel BC 1000 with deionized water were applied to them. Each of the three compresses was left on for 24 hours and then replaced by the next compress.

From the salt analyses of the compresses it could be seen, that the ions were extracted in about the same relative proportion as they were contained in the samples, i.e. none of the ions was significantly better extracted than the others.

Rather amazing was the fact, that the second compress in all cases (even in the samples containing no SAE) did lead to the extraction of more salts than the first compress (figure 3), this is in opposition to other experiences with similar compresses (see e.g. Grüner & Grassegger, 1993), and we do not have a final explanation for this. We suppose, that it has something to due with the fact, that our samples were placed in glass containers and not on porous systems.

The differences between the various consolidants did mainly show for the 10 % samples but also the 5 % samples did show similar trends. The smallest amount of salts could be extracted from the samples treated with Funcosil 300, which was the consolidant that performed best regarding to consolidation. The total amount of extracted salts lay between 200 mg and 1100 mg per dm^2 of surface area of the consolidated samples containing 5 % of salt (for full analyses see table 3 in the appendix).

5. 3 Conclusions from the laboratory experiments

Finally we decided to use Funcosil 300 as consolidant for the test area at St. Maria im Kapitol because after the three compresses the surface of sample 5a appeared to be in better condition than the surfaces of any of the other samples. An other reason for its selection was the fast and durable hardening of this consolidant (figure 2).

Although the salt extraction was more reduced by Funcosil 300 than by the other SAE, it was decided, that the consolidation effect to the renders and wall paintings was the most important criterion for the selection of the consolidant, as desalination always means some physical stress to the treated material.

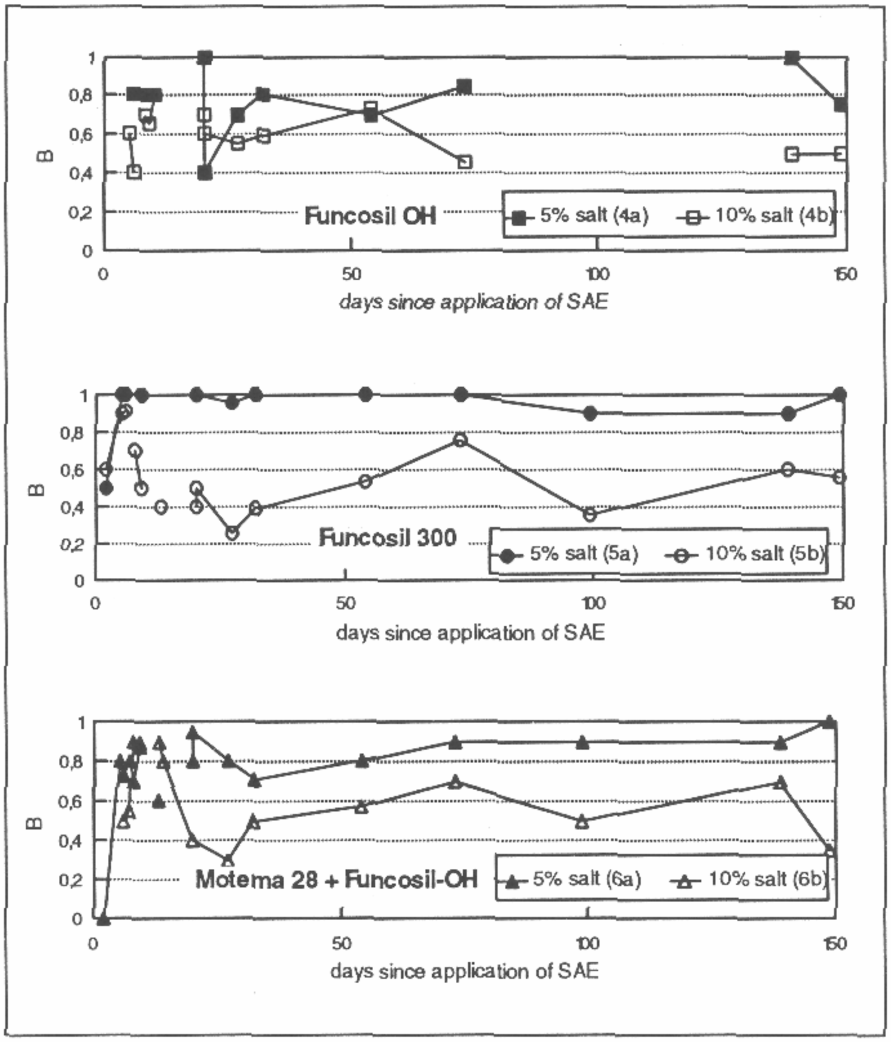


Fig. 2 - *B value from the "needle test" plotted against the days since the application of the consolidants,*

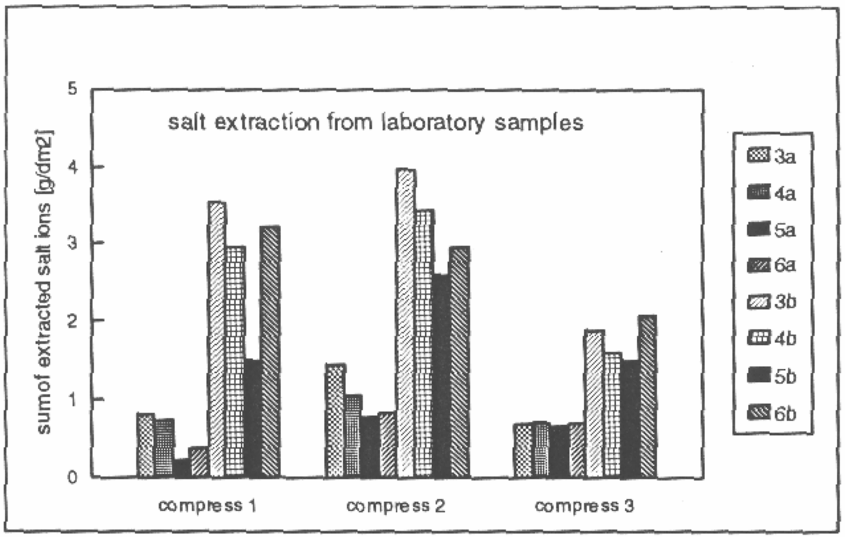


Fig. 3 - *Total amount of extracted ions from the laboratory samples. Sample 1b is not plotted, because of its too low content of salt ions (0.006 to 0. 008 g/dm^2).*

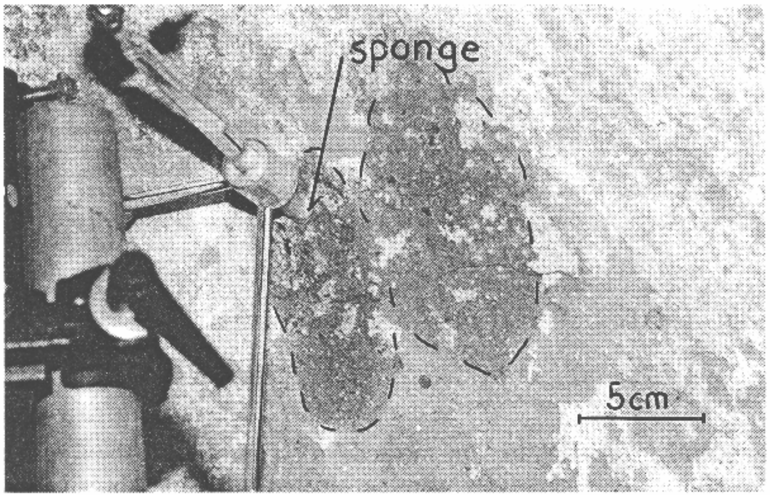
6. Application at the test area of St. Maria im Kapitol

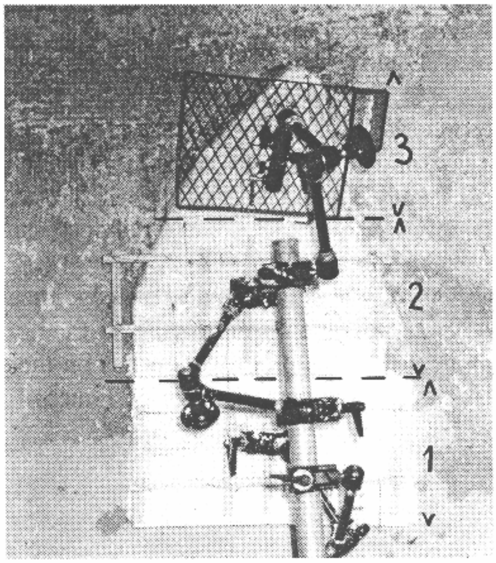
6. 1. Consolidation

All frequently used application methods for consolidants like spraying, using a paintbrush or compresses were considered to be too abrasive in our case, where the paintings could only be touched at a few spots. The application method was therefore specially developed. Analogously to the Mirowsky testing tubes for the measurement of liquid penetration into porous materials, we used glass tubes with a sponge, which served as contact point to the wall. The other end of the tube was connected by a flexible silicon tube to a container with the SAE supply. The consolidant was then sucked up through the sponge by the materials of the wall mainly due to capillary forces. The advantage of this method was, that with only a few contact points of about 1 cm^2, it did allow to impregnate oval areas of nearly one dm^2 near the sponge (fig. 4),

We used this time-consuming method, which is normally uneconomical, in order to have as little contact points as possible on the fragile surface of the painting. The method is very complicated, as its progress depends on the suction of the material, it took 7 days to have about 1.5 litres of Funcosil 300 applied to an area of about 0.5 m^2.

Two months after the treatment the surface of the testing area resisted much better to the sting of a needle than the untreated parts. The test field did not show alterations, with the exception that it appeared slightly darker than the surrounding parts. When applying little water drops to the render, they were immediately sucked away. By using this application method for the consolidant even strongly damaged parts of the painting, like loose hanging parts of the paint layer, could be saved. Some parts however were still in risk to get lost during desalination, they had to be fixed by a SAE to which was added some ammonia to enhance the reaction speed.





↑ **Fig. 4** - *Apparatus to apply the consolidant. The dashed lines mark the dark areas where the consolidant is being applied to or has been applied shortly beforehand.*

← **Fig. 5** - *Compresses with their mechanical supports at the test area in St. Maria im Kapitol.*

6. 2 Desalination

The desalination was carried out as for the laboratory tests by using cellulose compresses with deionized water. Arbocel BC 1000 a frequently used product for these purposes was used. Following the laboratory tests 18 g Arbocel per dm^2 were calculated to be needed. Four consecutive compresses were applied. The first was left on the wall for three days over the weekend and the following ones were each left at the wall for 24 hours. Because of the spherically inclined vaulting, the compresses had to be supported by flexible polyurethane plates, covered by plastic sheets (figure 5).

The compresses did not dry out at the wall, so that they were still quite humid when they were taken away, with the lower parts having a remarkably higher water content than the upper ones. Because of the supports, the compresses could be removed in big plates without breaking apart. This helped us, to control how much particles from the paintings were removed together with the compresses. With our method we could make sure that only very few material was accidentally removed from the paintings.

7. Results of sample analyses

Due to lack of time we were only able to analyse some of the compress material. Therefore the first two compresses from the two lower fields and the second compress of the third field were selected to be analysed. As the lower fields had been much wetter when the compresses were removed, we had expected, these compresses to contain more salt than the compresses of field 2 or 3, which however did not turn out to be true (see figure 6 and table 4 in the appendix).

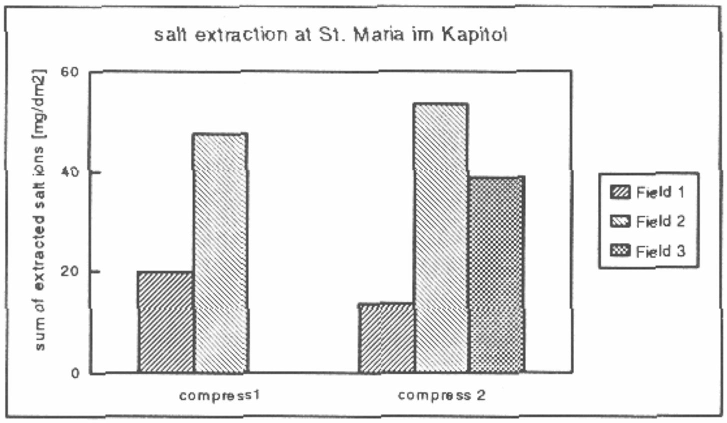


Fig. 6
- Total amount of extracted salt ions from in situ desalination.

The compresses led to the extraction of between 13 mg and 54 mg salt per dm^2 of surface from the wall paintings, which is up to 20 times less, than what was extracted in the laboratory tests. This has probably to do with the fact, that the material lying underneath the original renders is porous and could therefore suck away some of the applied water, and lead to a redistribution of the salts rather than to an extraction.

8. Conclusions

The laboratory tests were intended to be comparable to the situation at St. Maria im Kapitol in several ways. They should be performed on samples containing the same amount and mixture of salt and the samples should have the same fragile state. For the testing of the individual consolidants and their behaviour in a salt contaminated porous structure - the main aim of the reported work - these samples gave results which were very well comparable to the findings for the original renders. The laboratory work was therefore a very helpful tool for the decision making.

Regarding the quantitative salt analyses to monitor the success of the desalination procedure, the laboratory samples did give a picture which was very different from the analyses of the compresses that had been applied in situ. This can probably be explained by the fact, that at least some of the water was sucked away by the porous materials that lay underneath the original renders, but maybe also by the inhomogeneity of the original material.

It could nevertheless be clearly shown, that similar but different silicic acid ethyl esters did influence the possibility of desalination strongly, and that the consolidants themselves were also strongly influenced in their consolidating effect by the presence of salts.

To further test the possibilities of desalination of renders after the application of consolidants, it would be necessary to set up different laboratory tests, or to even find an ancient render where adequate test fields could be set up.

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Appendix
Description of the quantitative salt analysis

Mortar samples: 1 g of air dry sample was mixed with 100 ml of deionized water, then stirred for 1 minute and extracted over a 0.45 mm filter. The weight loss of the sample was measured as well as the pH and the electrical conductivity of the filtrate; sodium was analyzed by means of a sodium ion selective electrode; K^+ , Mg^{++}, Ca^{++}, $NH4^+$ *Cl-,* $NO3^-$ *and* $SO4^{--}$ *were analyzed by means of photometry (photometer Dr. Lange). All ionic contents were calculated to mg or mmol per gram sample respectively.*

Samples of desalting compresses: 5 g of air dry compress were mixed with 100 ml of deionized water, then stirred for 1 hour (!) and extracted over a 0.45mm filter. The weight loss of the sample was measured The analysis of the filtrate was done exactly as for the mortar samples, but the values were calculated to be given in mg or mmol per dm^2 *of surface area, as on the original paintings we could not possibly know how deep the desalting effect of the compresses would be.*

sample	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	Cl^-	NO_3^-	SO_4^{--}	Sum
1b/1	1'639	<2'200	2'145	283	6	3'781	354	<11'000	8'208
1b/2	l'247	<2'200	1'893	224	5	2'211	452	<11'000	6'032
1b/3	l'387	<2'200	2'077	314	18	l'520	532	<11'000	5'849
3a/1	70'851	43'620	96'798	20'329	29	166'540	374'652	20'980	793'799
3a/2	116'044	59'571	183'487	48'079	80	274'088	734'555	29'205	1'445'110
3a/3	53'795	30'366	94'301	18'564	56	125'211	343'966	15'112	681'371
4a/1	55'056	29'875	99'172	18'799	27	145'175	358'816	17'675	724'594
4a/2	73'324	3l'970	161'368	27'848	14	191'361	521'320	33'268	1'040'474
4a/3	49'135	23'968	107'096	20'121	54	125'982	359'005	22'133	707'492
5a/1	17'759	8'941	33'086	5'440	14	47'676	108'499	<11'000	221'415
5a/2	65'798	38'254	111'948	14'002	25	152'962	363'553	26'630	773'171
5a/3	47'027	24'492	99'684	19'023	44	119'339	34 l'996	17'079	668'684
6a/l	30'638	20'296	55'843	5'022	14	76'843	169'321	17'837	375'814
6a/2	71'199	41'856	117'356	12'607	14	161'910	385'289	27'859	818'092
6a13	49'664	26'598	103'199	19'865	42	127'633	350'606	13'441	691'048
3b/1	340'721	128'728	416'128	115'788	73	813'983	1'689'939	29'043	3'534'402
3b/2	724'594	155'633	512'611	145'989	50	785'277	2'020'797	32'947	3'972'167
3b/3	134'872	77'593	255'581	60'646	86	338'625	992'064	16'271	1'975'738
4b/1	272'772	113'659	416'196	68'662	77	645'146	1'420'000	29'872	2'966'384
4b/2	274'280	127'0 13	496'097	93'262	29	675'068	1'742'372	37'280	3'445'400
4b/3	111'155	66'370	223'186	47'168	80	282'690	836'770	17'421	1'584'842
5b/1	152'893	73'629	232'367	36'597	23	195'811	787'160	22'236	1'500'716
5b/2	222'989	105'473	370'984	59'832	63	544'709	1'253'498	33'666	2'591'214
5b/3	114'039	63'806	209'134	42'525	61	284'805	778'692	13'277	1'506'340
6b/1	287'047	125'333	452'122	76'402	81	694'648	1'545'190	33'977	3'214'800
6b/2	239'336	114'818	426'069	70'718	50	598'941	1'466'167	35'299	2'951'399
6b/3	137'832	79'237	268'172	60'155	56	353'982	1'165'153	19'059	2'083'647

Table 3 - Analyses *of the compresses of the laboratory samples. All values are given in [µg/dm^2].*
The number following the sample number indicates the number of the compress.

nr	**fld**	**Na$^+$**	**K$^+$**	**Ca^{++}**	**Mg^{++}**	**NH$_4^+$**	**Cl$^-$**	**NO$_3^-$**	**SO$_4^{--}$**	**sum**
1	1	<270	3'950	439	6'999	403	164	7'910	<11'000	19'866
2	1	2'383	<2'200	1'700	294	17	3'476	5'693	<11'000	13'564
1	2	<270	8'976	2'926	16'209	131	331	18'951	<11'000	47'525
2	2	4'457	<2'200	8'455	880	385	8'897	28'561	<11'000	51'635
2	3	3'611	<2'200	6'125	771	171	7'128	20'502	<11,000	38'308
blank >		561	<2'200	<540	<140	2	480	105	<11,000	1'148

Table 4 - *Analyses of the compresses that had been applied in situ.*
All values are given in [µg/dm^2]
(The very high ammonia contents are due to the use of ammonia see 6.1.)

Suppliers:

Motema 28; Interacryl, Schultheissenweg 105 c, D 60489 Frankfurt/Main

Funcosil OH and Funcosil 300; Remmers Chemie GmbH & Co, P.O. Box 1255, 49624 Löningen

Arbocel BC 1000; J.Rettenmaier & Söhne GmbH+CO, D 7092 Holzmühle über Ellwangen/Jagst

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