Electrode placement during electro-desalination of NaCl contaminated sandstone – simulating treatment of carved stones

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Abstract

Carved stone sculptures and ornaments can be severely damaged by salt induced decay. Often the irregular surfaces are decomposed, and the artwork is lost. The present paper is an experimental investigation on the possibility for using electro-desalination for treatment of stone with irregular shape with only two electrodes. The used Gotland sandstones were contaminated by NaCl in the laboratory. Due to the relatively good homogeneity in initial salt concentration obtained in this way, interpretation of the ED process were direct. Stones with an up-side-down T-shape formed the core of the investigation. Electro-desalination experiments were made with different duration to follow the progress. Successful desalination of the whole stone piece was obtained, showing that also parts not being placed directly between the electrodes were desalinated. This is important in case of salt damaged carved stones, where the most fragile parts thus can be desalinated without physically placing electrodes on them. The Cl removal rate was higher in the areas closest to the electrodes and slowest in the part, which was not placed directly between the electrodes. This is important to incorporate in the monitoring program to decide when a desalination action is finished.

Keywords: electro-desalination, sandstone, carved stone, NaCl

1. Introduction

Salt induced decay of historic carved stone, sculptural or ornamental, is a major cause for loss of important cultural heritage. Often the carvings making up the surface pattern are lost first, and thus these constitutes the most fragile parts. Poulticing is a group of used and discussed techniques for removal of salts from stone monuments. In these methods, a poultice is attached to all outer surfaces of the monument and the idea is to transport the salts from the stone into the poultice by diffusion and/or advection. However, in case of fragile carvings, poulticing can be difficult to apply, as these parts can further decompose by the physical contact. This paper is a laboratory investigation on the use of electro-desalination (ED) to remove salt from a sandstone with a T-shaped geometry, where the electrodes are placed in poultice around the simulated carving.

ED is based on application of an electric DC potential gradient to the salt contaminated stone. In the electric field, ions in the pore solution are transported by electromigration towards the electrode of opposite polarity, and hereby the ions from the damaging salts are transported out from the stone. The electrodes are placed externally on the stone surface in electrode compartments with poultice, and the ions from the salts concentrate in the poultice during the treatment. When the poultices are removed after the desalination, the ions of the salts are removed with them.

At both metallic electrodes there are pH changes due to electrolysis:

At the anode:
$$H_2O \rightarrow 2H^+ + \tfrac{1}{2} O_2 \,(g) + 2e^- \qquad (1)$$
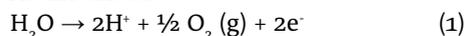
At the cathode:
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \,(g) \qquad (2)$$
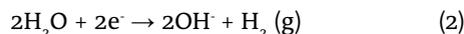
As seen from (1) and (2) pH decreases at the anode and increases at the cathode. It is necessary to neutralize the pH changes to prevent severe pH changes of the stone. The work by[1,2] underlined the importance of avoiding stone acidification, as in experiments without pH neutralization; the stones were severely damaged next to the anode. Use of a calcite rich clay poultice offers neutralization of the acidification from the anode.[3] The calcite buffers the acid and the clay gives workability, so the poultice can have optimal contact to the stone surface during the treatment.

Electro-desalination has been tested successfully in laboratory scale in different types of sandstones: Posta and Cotta sandstones[4], Gotland Sandstone[2], Nexø sandstone[5], and granite.[6] In fact no limit has been seen in stone type. Also successful removal of chlorides[4], nitrates[7] and sulphates[8] have been gained. These results were obtained with stone segments with plane surfaces. The present work focuses on the use of ED to desalinate carved stones.

Two works[9,10] have previously focused on ED of carved stones. Both these experimental works were carried out with stones, which had an uneven salt distribution, and both works confirmed that it was possible to extract salts from the elevated carvings of the stone, which were not placed directly between the electrodes. The uneven salt distribution in these stones, made interpretation of the result difficult. Further both investigations only included one experiment each, and thus the progress in desalination of the

carving needs to be clarified. The present paper is an experimental investigation, where T-shaped stone samples with a known and relatively even distribution of NaCl are desalinated from one set of electrodes.

2. Materials and methods

2.1. Stone for the experimental work

The experimental work was conducted with Gotland Sandstone, which is a stone type often carved in Denmark. The grey calcitic Gotland sandstone is composed of about 60 wt% quartz grains, cemented together by 7-10 wt% calcite, and with lower amounts of clay minerals, micas, feldspar minerals, pyrite, and glanconite.[11] The porosity is unusually large, around 15 % by volume.[11] This type of stone was chosen as it is commonly used and relatively homogeneous. T- shaped stone samples for the experiments were all cut from the same stone block, and had the same size, see *figure 1a*. To have a uniform distribution of the salt prior to the experiments, the stone samples were contaminated with the salt in the lab. The stone pieces were dried at 105°C and vacuum saturated by 80 g/l solution of NaCl in a desiccator prior to the ED experiments.

2.2. Electro-desalination experiments

Electrode compartments as seen in *figure 1b*. A frame was folded in thin plastic and jointed with tape to fit the horizontal part of the stone at each side of the attribute. The frames were filled with poultice; a mixture of kaolinite and $CaCO_3$ [3] with an initial water content of 54%. Inert platinum coated electrode meshes were placed at the top of each electrode compartment. The sandstone
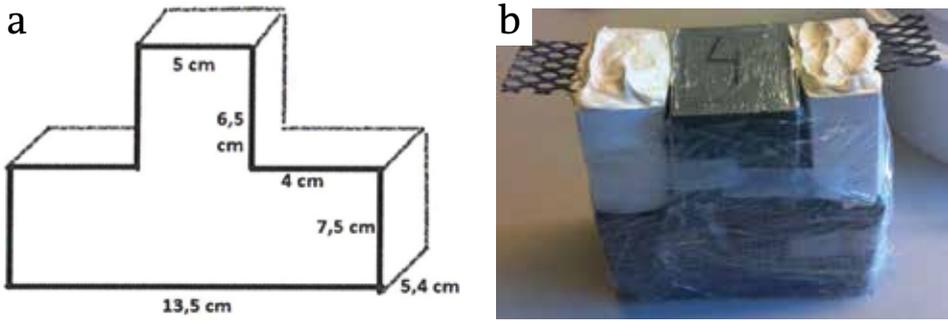
a

b

Figure 1: (a) The dimensions of the T-shaped stones and (b) The stone with electrodes.

and electrode compartments were wrapped in plastic film to hinder evaporation. A reference experiment (REF) was made with no applied current, but electrode compartments were placed at the stone exactly as in the ED experiments. The duration of the REF experiment was 7 days. Four ED experiments were made differing only in duration: 1, 4, 6 and 13 weeks (ED1, ED4, ED6 and ED13). A constant current of 10 mA was applied to the electrodes all through these experiments. *Table 1* shows the dry weight of the different stones, the water content after the vacuum saturation and the duration in weeks of the experiments.

After the REF and ED experiments, the stones were segmented with hammer and chisel into 16 segments *(Figure 2)*.

The water content in the segments was calculated as weight loss after drying at 105°C. The dried segments were grinded in a mechanical mortar. Following, 10 g powder was suspended in 25 ml distilled water and agitated for 24 h. The samples settled for 10 min and pH was measured. The samples were filtered through 0.45 μm filter. The Cl concentrations were analysed by ion chromatography (IC, Dionex DX-120).

The poultices were changed every 7 day except from ED13, where the last poultice was used in 3 weeks. The poultice was weighed, and Cl concentration, water content and pH were measured using the same methods as for the stone segments.

	Weight (g)	Initial water content (%)	Duration (weeks)
REF	1528	12.0	1 (no current)
ED1	1513	12.0	1
ED4	1536	11.6	4
ED6	1504	12.1	6
ED13	1481	11.9	13

Table 1: REF and ED experiments. Dry weight of stone, initial water content after vacuum saturation and duration of experiment

	Water content (%)	pH	Cl (mg/kg)
REF	10.4 ± 0.2	8.8 ± 0.06	4290 ± 530
ED1	9.9 ± 0.6	9.0 ± 0.9	4050 ± 1060
ED4	9.9 ± 0.3	10.8 ± 0.9	1580 ± 760
ED6	9.1 ± 1.1	11.3 ± 1.0	650 ± 500
ED13	3.0 ± 0.2	11.3 ± 0,9	21 ± 4

Table 2: Water content, pH and chloride concentration (average ± standard deviation) in the stone segments at the end of the REF and ED experiments
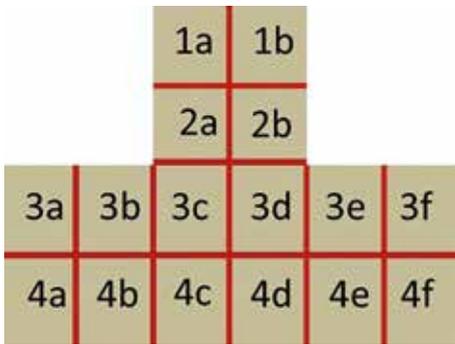

Figure 2: Segmentation and numbers after REF and ED experiments

3. Results and discussion

3.1. Overall results

Table 2 shows the overall results from the ED experiments as average values (± standard deviation) of water content, pH, Cl concentration. The water contaent was maintained at the same level when changing the poultice every week, but not if the same poultice was used for 3 weeks as was the case for the last poultice in ED13. The pH increased when the duration of ED was prolonged due to electrolysis at the cathode, which was not buffered sufficiently in the poultice. The Cl concentration decreases to a very low level in ED13.

3.2. Comparison of REF and ED1 experiments

Figure 3a and b shows respectively the resulting Cl concentrations in the different stone segments of the REF stone with poultice but without an applied electric field and in the corresponding ED1 experiment with poultice and applied electric field, both after 7 days.

The REF stone shows lower Cl concentration in the segments, which had direct physical contact with the poultice (segments 3a, 3b, 3e and 3f, *figure 2*). The Cl concentrations in the two REF poultices were 3600 and 4200 mg/kg. As the Cl concentration was non-measurable in the poultice before the experiment, the Cl was transported from stone to poultice during the 7 days of the experiment. In the same period, the water content in the poultice decreased from 53.6% to 47.3%. In addition, the average water content in the stone decreased from 12.0% *(table 1)* to 10.4% *(table 2)*. Thus, the wrapping of the stone and poultice did not fully hinder evaporation. The possible transport mechanisms for Cl from stone to poultice are diffusion and advection. Calculating the pore water concentration of Cl in the two materials based on stone concentration and water content, the pore water concentration in the stone (41 g/l in aver-
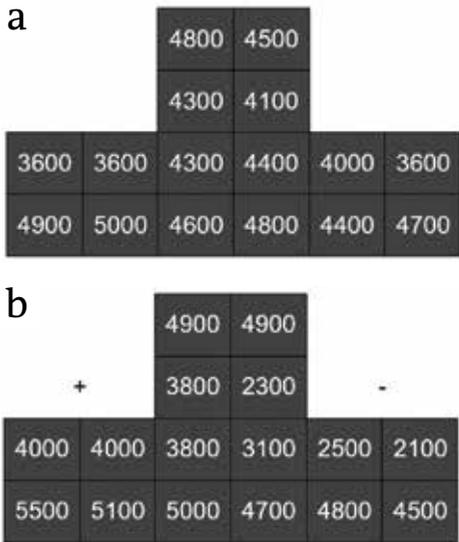
a

		4800	4500		
		4300	4100		
3600	3600	4300	4400	4000	3600
4900	5000	4600	4800	4400	4700

b

		4900	4900		
+		3800	2300	-	
4000	4000	3800	3100	2500	2100
5500	5100	5000	4700	4800	4500

Figure 3: Chloride concentrations in the segment of the (a) REF stone and (b) and in the segment of the ED1 experiment after 7 days [mg/kg]

age) is much higher than in the poultice (8.3 g/l), and thus the concentration gradient between the two allows a continued diffusion. Whether the drying of the poultice and stone transport water from stone to poultice cannot be assessed on basis of the current data, however, this transport must be considered limited, and thus advection is not considered as being of major importance.

Due to the applied electric field, the Cl concentration pattern in the ED1 stone differs from the REF *(figure 3b)*. As Cl-electromigrates from the cathode end towards the anode, the concentration in the stone segments, which were in direct contact with the cathode poultice (3e and 3f) were lower than the concentration in 3a and 3b (in the anode end). The concentration in 3d and 2d are clearly decreased as well. The latter shows that the electric field lines distributed into the attribute already during the first week of ED. The Cl concentrations in the anode and cathode poultices were 7670 mg/kg (cathode) and 250 mg/kg (anode), which are higher and lower than the concentration in the poultices in the REF experiment, respectively.

3.3. Cl removal from stone over time during ED experiments

Figures 4a, b and c show the Cl concentrations in the different segments *(figure 2)* of the ED experiments over time. Together these figures illustrate how the desalination progresses in the stone works. The Cl concentration decreased over time in all segments and a very low level of below 30 mg Cl/kg was obtained in every segment in ED13. Thus a very important conclusion can be drawn. It is possible fully to desalinate such attribute by ED.

The removal rate differed in the different segments. *Figure 4a* show that the Cl removal was fastesr in the segments in row 2 than in row 1, i.e. the desalination occurred from the row closest to the electrodes first and later to the upper row. The same pattern is seen when comparing the desalination of row 3 *(figure 4b)* and row 4 *(4c)* when e.g. comparing the Cl concentrations after 6 weeks in the two figures. In row 3 the concentrations were less than about 500 mg/kg and in row 4, the concentrations were all higher than 500 mg/kg. That row 3 is desalinated before row 4 confirms the pattern found for ED of bricks in[3], when the electrodes were placed at the same side of the bricks. Further, it is evident that the Cl concentration decreased fastest from the end of the stone closest to the cathode *(figures 4a and b)*, e.g. 3f and 4f had.

From the Cl concentration and weight of poultice measured every week (when the poultices were changed) the accumulated Cl removal over time can be calculated. *Figure 5* shows the Cl removed into the anode poultice. The Cl removal in the four ED experiments progresses very similar and as discussed in section 3.2, the
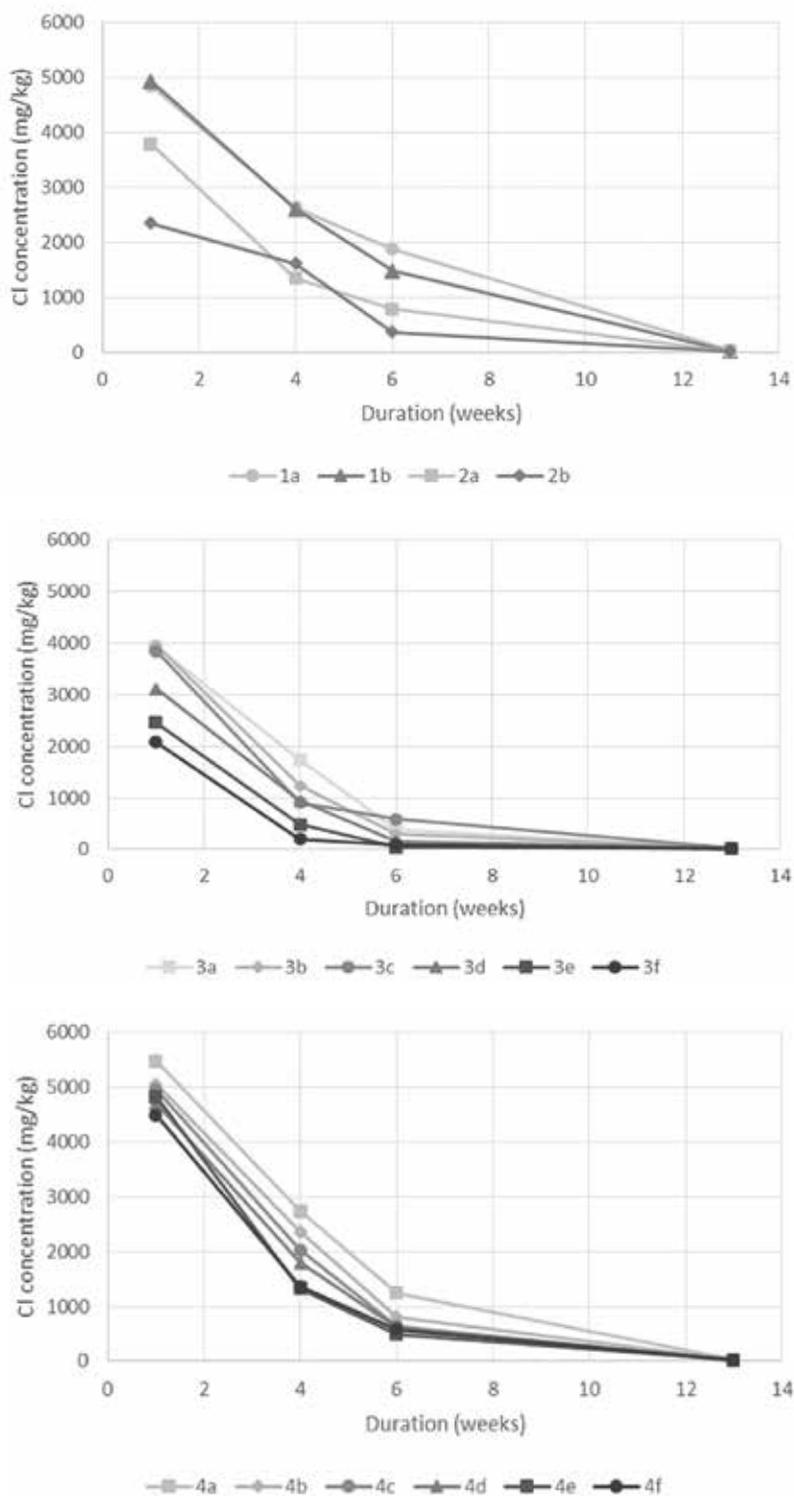
Figure 4: Cl concentration in the different stone segments as function of ED duration: (a) in the attribute, segments in row 1 and 2 (b) segments in row 3 and (c) segments in row 4.

removal into the anode poultice is about double the concentration in the REF experiment during 1 week.

During the first 3-4 weeks, the accumulated Cl removal in the ED experiments increases almost linearly with duration. Between 4 and 9 weeks, the removed amount of Cl decreases every week and after 10 weeks the removal is very low. This pattern corresponds well to the results in *figure 4*, where it is seen that after 6 weeks, the concentration is lowered significantly in every segment. However, combining the two experiments also show, that it is important to continue the ED of the carved object after the point where the Cl removal rate into the poultice decreases. Evaluating the ED only on basis of figure 5 could mislead to the conclusion that the desalination was sufficient after 6-7 weeks, but *figure 4a* shows, that at this point the Cl concentration is still rather high in segments 1a and 1b. Thus in the case of ED treatment of sculptures and ornaments, the progress of the

desalination must be followed also by other means to ensure full desalination

The total amount of Cl into the anode poultice was 3300 mg Cl *(figure 5)* and for comparison, only 65 mg Cl was removed into the cathode poultice. This underlines the effect of the applied electric field.

4. Conclusions

This investigation shows that ED has potential to desalinate carved stone, as the salts can be removed from parts, which are not directly between the electrodes. In the present investigation, T-shaped stones were fully desalinated using two electrodes from an initial concentration of about 4300 mg Cl/kg to about less than 34 mg Cl/kg in all parts of the stone. The part not situated directly between the electrodes was desalinated with the slowest rate, and the Cl amount removed into the anode poultice decrea-
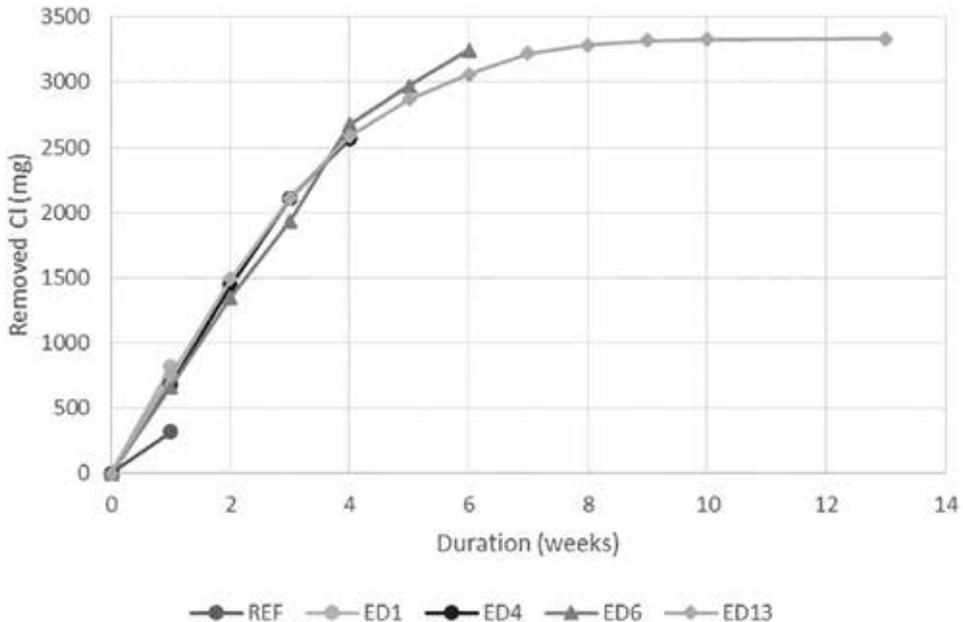

Figure 5: Accumulated Cl amount removed into the anode poultice during the REF and ED experiments.

sed to a very low overall level during while this part was desalinated. Thus it cannot be assessed whether the desalination is finished only on basis of the removal rate into the poultice at the electrodes.

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