

Electro-Desalination of Sandstones With Cracks

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Abstract. *Historical stone monuments and buildings are lost due to salt induced decay. This paper deals with a method, electro-desalination (ED), in which an electric DC field is applied to the infected stones. The method utilizes that ions are transported (electromigrating) in the pore solution in the electric field. In the experimental work here, sandstone prisms were spiked with NaCl to high concentrations prior to ED. During the application of current, the Cl ions are electromigrating into a poultice at the anode, and Na ions into a poultice at the cathode. Damaged stones are often fragile and cracked, and the focus of this paper is to investigate experimentally if the salts are removed effectively from the stone parts next to a crack. In the lab experiments performed, a crack was cut half through the rectangular sandstone prisms perpendicular to the electric field. The results showed no delay on the ED process from the crack. All through the stone, very low concentrations of Na and Cl were reached. The concentration were even lower than the concentrations before the spiking. This finding of effective desalination around a crack is important, as it means that during ED, the poultice with electrodes can be placed around the cracked and fragile surfaces, and thus further damage from physical contact between poultice and fragile stone can be avoided.*

Keywords: *Salt Induced Decay, NaCl, Sandstone, Electro-Desalination, Historical Buildings.*

1 Introduction

Soluble salts cause damage to many historic stone buildings and monuments, and cultural heritage is lost. When water accesses the pore network of a stone, it may carry various salts in solution. Several mechanisms can subsequently cause crystal growth and crystallization-dissolution cycles, which can result in severe stone damage. The techniques to remove the damaging salts are few, and an overall effective method is lacking. The use of poultice materials to reduce the salt content of salt deteriorated objects is a long established technique in conservation (Sawdy-Heritage *et al.*, 2008). However, due to the complex nature of salt problems within historic structures the result of such interventions can be variable and unpredictable. The amount and depth to which salts are mobilised, and where they are transported to, is dependent on the inter-relationship between the poultice and the substrate, the drying conditions and also the initial salt distribution (Sawdy-Heritage *et al.*, 2008).

Another option is electro-desalination (ED), which is a method under development. ED is based on application of an electric DC potential gradient to the salt contaminated stone. The method utilizes that ions in the pore solution are transported by electromigration towards the electrode of opposite polarity when the electric field is applied. 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 ED, the ions of the salts are removed with them.

Electrolysis of water occurs at both metallic electrodes: at the anode $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 (\text{g})$

+ 2e⁻ and at the cathode 2H₂O + 2e⁻ → 2OH⁻ + H₂(g). As seen, pH decreases at the anode and increases at the cathode. It is necessary to neutralize the pH changes to prevent severe damage of the stone. The work by (Herinckx *et al.*, 2011; Skibsted, 2013) underlined the importance of avoiding stone acidification, as in ED 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 (Rörig-Dalgaard, 2013). The calcite buffers the acid and the clay gives workability, so the poultice can have optimal contact to the stone surface during the treatment.

Previous research has shown that ED can be removed from high and damaging concentrations to very low concentrations in laboratory scale from different types of sandstones: Posta and Cotta sandstones (Ottosen and Christensen, 2012), Gotland Sandstone (Skibsted, 2013), Nexø sandstone (Pedersen *et al.*, 2010), and granite (Feijoo *et al.*, 2013). No limitation posed by the stone type has been reported. Also successful removal of different salts of chlorides (Ottosen and Christensen, 2012), nitrates (Skibsted *et al.*, 2013) and sulphates (Ottosen, 2016) have been obtained.

An advantage of ED over poulticing is that whereas in poulticing the poultice needs to be covering the surface of the object, inclusive the most fragile parts, this is not necessary in ED. In ED, the poultice with electrodes can be placed around the fragile parts, and the electric field will distribute into the stone material. It has been shown experimentally that the salts can be removed from stone parts, which are not placed in the direct line between the electrodes, which means that e.g. carvings can be desalinated (Ottosen *et al.*, 2014 ; Feijoo *et al.*, 2017; Ottosen, 2017).

Damaged stones are often cracked, and thus it is relevant to investigate if the salts are removed efficiently around the cracks. The electric field can pass only through the moisture of the pores and in case the crack is air-filled, it acts as an insulator, which the electric field lines cannot pass. This work is an experimental investigation of the influence from a major crack on the ED process. Laboratory experiments are conducted with single sandstones, where a major crack is cut perpendicular to the electric field lines, and the salt concentration around the crack is measured after different durations of the desalination.

2 Materials and Methods

2.1 Experimental Stones

The experimental work was conducted with Gotland Sandstone. This type of stone was chosen, as it is relatively homogeneous and it is commonly used in Denmark. All sandstone pieces in this work were cut from the same block.

2.2 Measuring Techniques

For the measurement of pH, conductivity and concentration of soluble Cl and Na, the dried stone samples 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. Na concentrations were measured by ICP-OES. Cl concentrations were measured by ion chromatography (IC, Dionex DX-120). The concentrations for each segment was measured as single determination.

The open porosity and density of the Gotland Sandstone used in this work were determined (five replicates). Sandstone pieces of 170-190 g were dried (105 °C for 24 hours), weighed (m_{dry}), and placed in a desiccator under vacuum for approximately 3 h. After 3 h, distilled water at room temperature was led into the desiccator, so that the discs were completely submerged. Vacuum was maintained for 1 h. Hereafter, air was let into the desiccator and the submerged discs were left at atmospheric pressure overnight. The water-saturated pieces were weighed in water (m_{sw}) and in air after wiping excess water of the surface (m_{sa}). The open porosity was calculated as $\left(\frac{m_{\text{sa}} - m_{\text{dry}}}{m_{\text{sa}} - m_{\text{sw}}}\right) * 100\%$; and apparent density $\left(\frac{m_{\text{dry}} * \rho_w}{m_{\text{sa}} - m_{\text{sw}}}\right)$, where ρ_w (970 kg/m³) is the density of water.

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 prisms were dried at 105°C and vacuum saturated by 80 g/l solution of NaCl in a desiccator prior to the ED experiments. The dry weight of the stone prisms before vacuum saturation (m_d) and the stone weight after vacuum saturation (m_0) were measured and from these the initial water content was calculated as $(m_0 - m_d)/m_d * 100\%$.

2.3 Electro-Desalination Experiments

Four rectangular stone prisms were cut from the same stone block. The prisms were 13.5 cm x 7.5 cm x 5.5 cm. A crack was cut half way through each prism in the middle, perpendicular to the longest side (and the electric field lines) (Figure 1). The width of the void was about 1 mm.

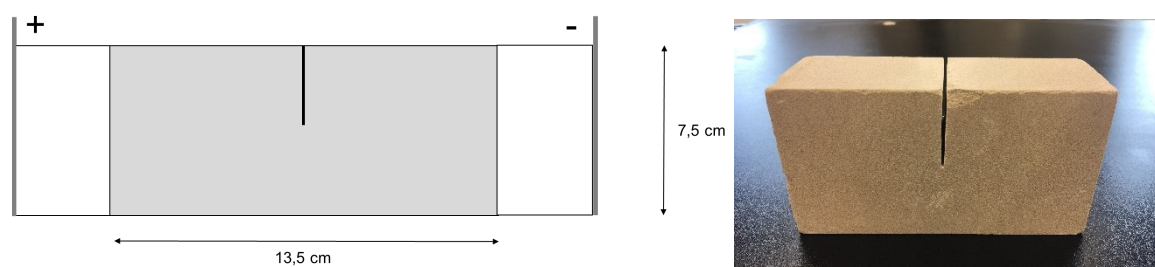


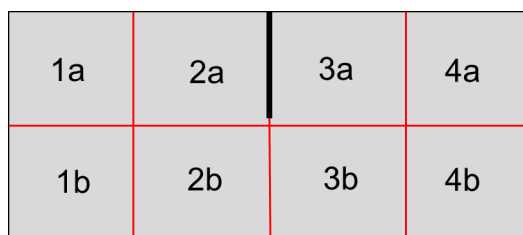
Figure 1. The setup for electro-desalination. The electrodes are placed in clay poultice on each end of the stone, and a crack is cut half into the stone perpendicular to the electric field.

Electrode compartments were placed at each end of the rectangular stone prism as illustrated in figure 1(a). For the electrode compartments a frame was folded in thin plastic to fit the surface of the stone at each side. The frames were filled with poultice; a mixture of kaolinite and CaCO₃ [3] with an initial water content of 54%. Inert platinum coated electrode meshes were placed at the end of each electrode compartment. The sandstone and electrode compartments were wrapped in plastic film to hinder evaporation. A reference stone (REF) was made with no applied current. The REF stone was wrapped in plastic film for 14 days. Three ED experiments were made differing only in duration: 2, 4 and 5 weeks (ED₂, ED₄ and ED₅). A constant current of 10 mA was applied to the electrodes all through these experiments. Table 1 shows the dry weight (m_d) of the different stone prisms, the water content after the vacuum saturation and the duration of the experiments in weeks.

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

	Stone weight, m_d (g)	Initial water content (%)	Duration (weeks)
REF	1072	10.2	2 (no current)
ED ₂	1056	10.4	2
ED ₄	1084	10.5	4
ED ₅	1079	9.4	5

After the REF and ED experiments, the stone prisms were segmented with hammer and chisel into 8 segments (Figure 2). The upper row of segments were named a-segments and the lower b-segments. All segments were weighed and dried (24 hours at 105°C), and the water content calculated. The dried segments were grinded in a mechanical mortar (FRITSCH – pulverisette 9) for 10 seconds. 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 analyzed by ion chromatography (IC, Dionex DX-120).

**Figure 2.** Segmentation of stone block after electro-desalination.

The poultices were changed every 7th day. The poultices were weighed. The Cl and Na concentrations, water content and pH were measured using the same methods as for the stone segments.

3 Results and Discussion

3.1 Characteristics of the Sandstone

The porosity of the Gotlandic sandstone used in the experimental work was $20.4\% \pm 0.03\%$, which is higher than previously reported (15%) by (Nord and Tronner, 1995). The difference shows a natural variation in the porosity of Gotlandic sandstone. Nord and Tronner (1995) reported that 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 glauconite.

The concentrations of Cl and Na before and after spiking with NaCl is shown in table 2 together with pH and conductivity. The salt concentration is similar to previous investigations with the same type of sandstone and concentration of NaCl in the spiking solution (Ottosen *et al.* 2014).

Table 2. Concentrations of Na and Cl, pH and conductivity of the stone before and after spiking with NaCl.

	Na (mg/kg)	Cl (mg/kg)	Conductivity (mS/cm)	pH
Before spiking	23.3 ± 0.3	21.4 ± 4.2	0.46 ± 0.04	8.6 ± 0.04
After spiking	2520 ± 230	4200 ± 130	5.33 ± 0.16	9.1 ± 0.1

3.2 Electro-Desalination Results

The concentrations of Cl and Na in the different segments after the REF and the three ED experiments are shown in figure 3. The decrease in concentrations is clear and the average concentrations were already about halved after two weeks.

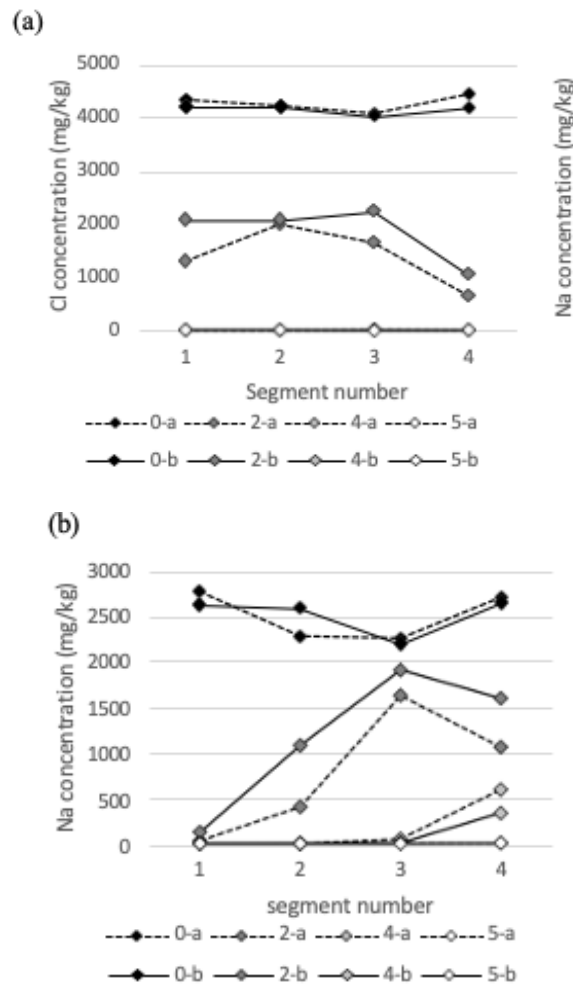


Figure 3. Concentration profiles of (a) Cl and (b) Na in the stone segments at the end of the experiments. The dotted lines are the profiles in the segment row with the crack (a-segments) and the full lines are the lower row of segments (b-segments).

The final Cl concentration in all segments in ED₄ was between 14 to 19 mg Cl/kg (figure 3), which corresponds to a reduction of more than 99.5% in comparison to the 4200 mg Cl/kg, which was the initial concentration in the ED experiments (Table 2, concentration after spiking). The final Cl concentrations were even lower than the concentration in the stone before the spiking (21.4 mg Cl/kg; table 2), and the Cl removal was successful all through the stone. Thus, the final Cl concentration in the segments next to the crack was not negatively influenced by the crack.

The Na removal was not finished in ED₄ since the concentration was still 340 and 600 mg Na/kg in the segments closest to the cathode, 4a and 4b, respectively (figure 3). Thus, the removal of Na was slightly slower than the removal of Cl. However, within one week longer treatment, the Na removal was successful, as in ED₅ the concentrations in the segments were between 7 and 11 mg Na/kg, which was also less than before the spiking (2520 mg Na/kg).

The successful desalination was supported by the conductivity, which in the segments after ED₅ was 0.096 ± 0.007 mS/cm was also less than the 0.46 ± 0.04 mS/cm prior to the spiking.

The pH in the segments after ED₅ was between 9.7 and 10.3. Since the initial pH was 9.1 (table 2), the pH was increased all through the stone, and the acidic front was thus prevented in developing into the stone by the poultice.

In summary, Na and Cl were removed to very low concentrations in all stone segments during the ED treatment and after 5 weeks, the concentrations were lower than before the stones were spiked. Thus, the crack did not prevent successful desalination.

Results from experiment ED₅ are in figure 4 as the accumulated moles of Cl removed into the poultice at the anode and Na into the poultice at the cathode. The number of moles were calculated from concentrations measured in the poultices when they were changed every 7 day. In figure 4, the electrical resistivity is shown as well (calculated as voltage divided by current). During the first approximately three weeks, the removed mass of Cl and Na is almost linear with the duration of the treatment, and in this period, the electrical resistivity is very low. After about 3 weeks, the removal rate decreased as result of a lower concentration of the ions in the stone. After a little more than 3 weeks of treatment, it is also seen that the electrical resistivity increases dramatically corresponding to the low level of removal indicating lower salt content left in the stone. Thus, the time for the desalination to be finished is indicated by an increase in electrical conductivity.

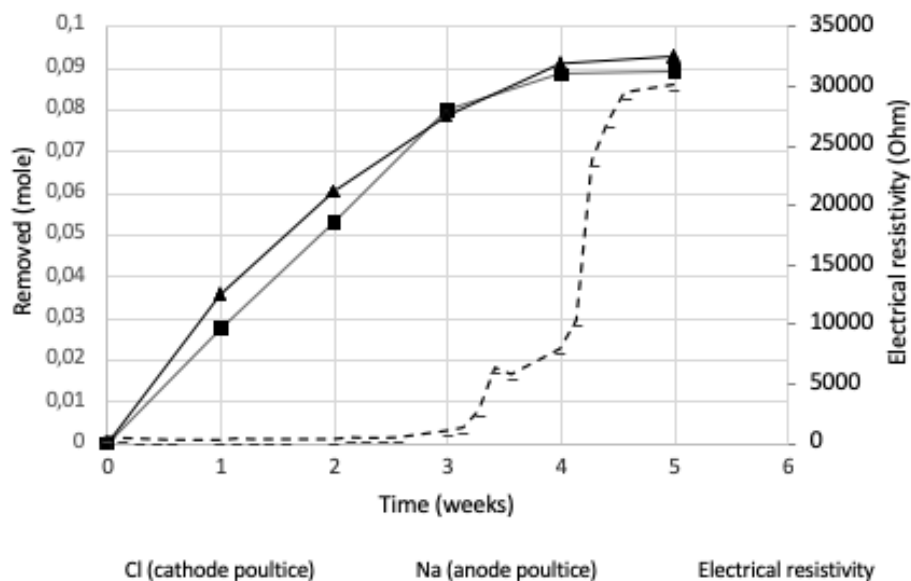


Figure 4. Number of moles Cl removed into in the anode poultice and Na into the cathode poultice over time in experiment ED₅. The electrical resistivity over time in ED₅ is shown as well.

4 Conclusions

Electro-desalination was experimentally shown to effectively remove Na and Cl from stone parts next to a crack. A crack was cut half through rectangular sandstone prisms (13.5 cm x 7.5 cm x 5.5 cm) and electrode compartments were placed in each end of the prism. The prisms were spiked with NaCl to high concentrations prior to the electro-desalination, and after 5 weeks of treatment, the salts were removed again and even to concentrations lower than present in the stone prior to the spiking. The concentrations in the stone next to the crack were as low as in the other parts of the stone, and thus the interference of the crack on the overall desalination is minor.

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