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Ottosen, Lisbeth M.

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# ELECTRO-DESALINATION OF SULFATE CONTAMINATED CARBONACEOUS SANDSTONE – RISK FOR SALT INDUCED DECAY DURING THE PROCESS

L.M. Ottosen<sup>1\*</sup>

## Abstract

Sodium-sulphate is known to cause severe stone damage. This paper is focused on removal of this salt from carbonaceous sandstone by electro-desalination (ED). The research questions are related to possible stone damage during ED and subsequently suction cycles are made in distilled water before, during and after ED. During suction in water the salts are concentrated in the upper part of the sandstone. After 2 days of treatment the average water soluble  $\text{SO}_4^{2-}$  concentration was half the initial and for this sample corners were damaged as was the case for the reference stone. After 4 days of ED the average  $\text{SO}_4^{2-}$  concentration was 15% of the initial, and here no stone damage was seen from the suction cycles. This result shows that the damaging salts are removed and that no new harmful salts are formed during ED in the actual case. Acid is produced at the anode during ED. The acid is buffered in the poultice with carbonate. The acid would be highly damaging to the carbonaceous sandstone as the binder- $\text{CaCO}_3$  is soluble in acid. From *pH* measurements of the poultice it seems as if the acid is buffered well, as *pH* is still slightly alkaline after ED, but this is a measurement of the average *pH* and thus it was decided to measure the compressive strength of the stones after ED. The lowest compressive strength was measured for the reference stone, which had not been treated by ED (but had the highest salt content). Thus from this investigation there is an indication, that dissolution of carbonates in the stone did not happen, though the data material is too scarce to make a final conclusion. In summary, this investigation did support that ED removes the salts without new damaging side effects in the stone.

**Keywords:** electro-desalination, salt decay, sulphate, sandstone

## 1. Introduction

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 damaging effect varies between salts and salt mixtures, and not all salts are equally harmful, e.g. Rodriguez-Navarro & Doehne (1999) showed that evaporation from a saturated  $\text{Na}_2\text{SO}_4$  solution caused more damage in limestone than evaporation from a saturated  $\text{NaCl}$  solution, because  $\text{Na}_2\text{SO}_4$  easily forms supersaturated solutions, which is a mechanism for the generation of stress (Steiger & Asmussen 2008). According to Price and Brimblecombe (1994), at 20°C  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is

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<sup>1</sup> L.M. Ottosen\*

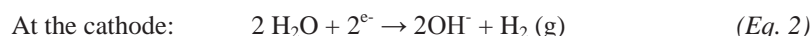
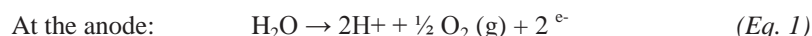
Department of Civil Engineering, Technical University of Denmark, Brovej, Building 118,  
2800 Kgs. Lyngby, Denmark  
LO@byg.dtu.dk

\*corresponding author

the stable form of sodium-sulphate at relative humidity (*RH*) between 71 % and 93 %.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  occupies a 314 % larger volume than the anhydrous salt. Thus the volume of sodium-sulphate changes significantly with changes in *RH*, which is likely to be a major factor involved in the development of crystal pressure. The topic of the present paper is removal of  $\text{Na}_2\text{SO}_4$  from carbonaceous sandstone by electro-desalination (ED).

The carbonaceous sandstone is Gotlandic sandstone, a soft, grey stone with approximately 20 % porosity and a fairly high degree of homogeneity, which makes it suitable for sculptures. The sandstone is sensitive to outdoor conditions due to the quite high porosity and the  $\text{CaCO}_3$  bonding. The calcite can chemically be transformed to gypsum when exposed to acid-rain (Suneson 1942). Based on samplings from two monuments built of Gotlandic sandstone Nord and Tronner (1995) observed that rain dissolved calcite and decreased the Ca concentration in the stone. The dissolved Ca concentrated at the surface where a hard, thin gypsum crust was formed.

ED is based on application of an electric potential gradient and electromigration of the ions from the damaging salts out from the stone. During ED electrodes are placed externally on the surface of the salt infected stone. The electrodes are placed in a poultice in which the ions from the salts concentrate during the treatment. When the poultices are removed after the desalination, the ions of the salts are removed with them. At both electrodes there are *pH* changes due to electrolysis reactions:



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. Herinckx *et al.* (2011) and Skibsted (2014) underlined the importance of avoiding stone acidification, as in experiments without *pH* neutralization; the stones were severely damaged next to the anode. Calcite rich clay poultice can be used for neutralization of the *pH* changes at the electrodes (Rörig-Dalgaard, 2009). The calcite buffers the *pH* changes and the clay gives workability, so the poultice can have optimal contact to the surface of the object to be desalinated. When the calcite buffers the acid from the anode,  $\text{Ca}^{2+}$  ions are released. If these ions do not precipitate with anions, they can be transported into the limestone by electromigration, and possibly precipitate with dissolved  $\text{SO}_4^{2-}$ . Should this happen, it may hamper the desalination and the formation of calcium- sulphates may even contribute to further salt weathering. In the present work it is investigated whether the stone is weakened during ED or at increased risk for salt decay during the process.

## 2. Materials and methods

### 2.1. Stone for the experiments

The Gotlandic stone pieces for the investigation were cut out of a former window frame from Kronborg Castle, Denmark. The original window frame had been removed and replaced during a renovation action. The outer parts of the stone were discharged, and the stone pieces for the experimental work (size 2.8×2.8×5.2 cm) were cut as seen in Fig. 1. The stone pieces were dried at 105°C. The pieces were vacuum saturated by 30 g/l  $\text{Na}_2\text{SO}_4$  in a desiccator prior to the ED experiments.

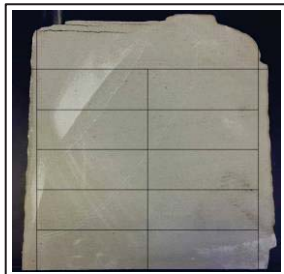


Fig. 1: The stone pieces were cut from a removed window frame.

### 2.2. Stone characterization

Two extra sandstone pieces were cut from the window frame ( $4 \times 4 \times 5 \text{ cm}^3$ ) for measurement of capillarity, porosity and density. Capillarity: The samples were dried at  $105^\circ\text{C}$ . The dry samples were weighed and placed in a tray with distilled water with 5 mm height on the stone. The sandstones were weighed after 1, 2, 4, 6, 8, 16, 30, 60, 120, 180, 240 and 360 min. The samples were dried at  $105^\circ\text{C}$  again. They were vacuum saturated in a desiccator and the stones were weighed above and below water as it is required to calculate porosity and density.

### 2.3. ED experiments

Electrode compartments with the size  $3 \times 3 \times 3 \text{ cm}^3$  were placed at each end of the sandstone piece (Fig. 2A). The frame of the electrode compartments were folded in thin plastic and jointed with tape to fit the ends of the stones. The frames were filled with poultice; a mixture of kaolinite and  $\text{CaCO}_3$  (Rörig-Dalgaard, 2009). Inert electrode meshes (electrodes, which do not take part in the electrode processes themselves) were placed at the end of each electrode compartments, see Fig. 2a. The sandstone and electrode compartments were wrapped in plastic film to hinder evaporation. A constant current of 2 mA was applied. The durations of the ED experiments were 2, 4 or 7 days (denoted ED<sub>2</sub>, ED<sub>4</sub> and ED<sub>7</sub> respectively).

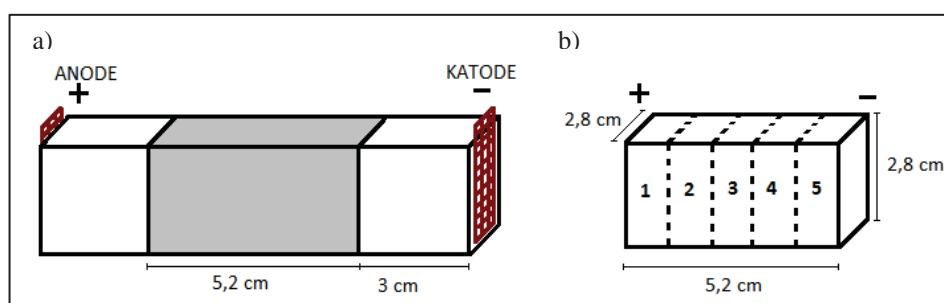


Fig. 2: a) ED setup with clay poultice and electrode mesh; b) segmentation of the stone after ED.

Each of the ED experiments was made in doublet. Concentration profiles were made on basis of one set of experiments, whereas suction cycles and compressive strength tests were made with the other set to evaluate the salt damage. See procedures below.

### 2.3.1. ED and concentration profiles

After ED the stones were segmented with hammer and chisel into five segments; numbered from the anode end (Fig. 2b). A reference stone (Ref.) was segmented directly after vacuum saturation by 30 g/l Na<sub>2</sub>SO<sub>4</sub> to get the concentration profiles before ED. The water content in the five segments was measured and calculated as weight loss after drying at 105°C per dry weight. 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. Na concentrations were analysed by ICP-OES. SO<sub>4</sub><sup>2-</sup> (and for the reference sample also Cl) concentrations were analysed by ion chromatography (IC, Dionex DX-120). For each segment the concentrations were measured as double determinations.

### 2.3.2. ED and stone decay

The present experimental work focuses on stone decay caused by calcium sulfate formed during ED and since this salt has a low solubility it will not necessarily be seen in the concentration profiles measured in the suspension of powdered sandstone in water. Thus it is necessary to evaluate the ED process based also on the decay pattern. Two drying/wetting cycles were performed just after ED: the stone pieces were dried to constant weight at 50°C. They were placed in distilled water to a height of 1 cm (Fig. 3). The surface where the cathode poultice had been placed was placed in the water. The water level in the beaker was kept constant manually. When water had been sucked all the way through the stone piece, the stones were left for 1 day in the setup. The stones were dried again to constant weight at 50°C and the suction procedure was repeated. After the second suction was completed, the stone pieces were inspected visually and compressive strength tests were performed.



Fig. 3: Suction test after ED.

### 3. Results and discussion

#### 3.1. Porosity, density and capillarity

The porosity of the experimental stone is 20.5% and the dry density 2120 kg/m<sup>3</sup>. In less than 2 hours water is sucked into the stone to full height (5 cm) and stable water content. The capillarity of the sandstone is high 5.98 kg/(m<sup>2</sup> s<sup>1/2</sup>).

#### 3.2. Removal of Na and SO<sub>4</sub><sup>2-</sup> during ED

The Gotlandic stone for the investigation had been exposed to the outdoor environment at Kronborg Castle, which is situated just next to Øresund with salt water. As the stones thus potentially can be infected by Cl, the concentrations of Cl were measured in the five segments of the reference stone: 60.2 ± 7.2 mg Cl/kg. Thus the Cl concentration of the stone pieces for the ED experiments is low and thus the major salt is the Na<sub>2</sub>SO<sub>4</sub> in which the stones were submerged.

Fig. 4 shows the concentration profiles of SO<sub>4</sub><sup>2-</sup> and Na through the stone piece at the end of the ED experiments. It is seen, that SO<sub>4</sub><sup>2-</sup> electromigrated towards the anode and Na towards the cathode, as it could be expected. The initial concentrations (Ref.) were 1950 ± 35 mg SO<sub>4</sub><sup>2-</sup>/kg and 940 ± 80 mg Na/kg. At the end of ED<sub>7</sub> the concentrations were decreased to 36 ± 4 mg SO<sub>4</sub><sup>2-</sup>/kg and 49 ± 5 mg Na/kg. This corresponds to removal percentages of 98% SO<sub>4</sub><sup>2-</sup> and 95% Na during 7 days.

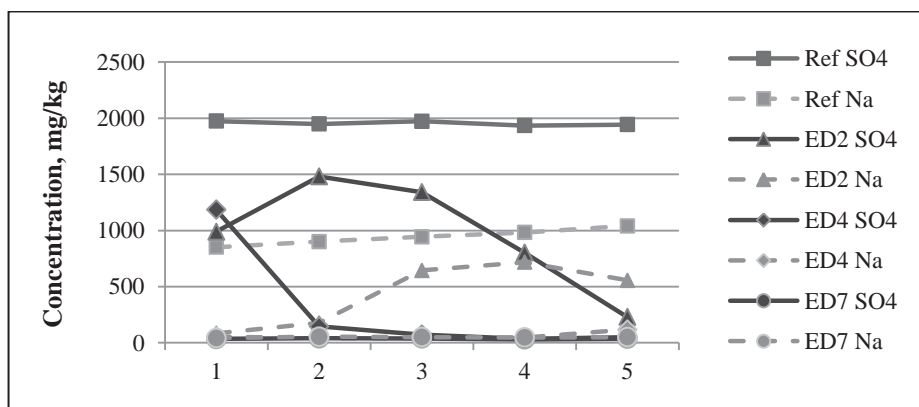


Fig. 4: SO<sub>4</sub><sup>2-</sup> and Na concentration profiles of Ref and ED stones.

Skibsted *et al.* (2015) reported that the ED removal rate per valence for SO<sub>4</sub><sup>2-</sup> was 75% of the ED removal rates for Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> regardless the ionic mobility of SO<sub>4</sub><sup>2-</sup> is slightly higher than that of the monovalent anions. The main reason for the lower removal rate for SO<sub>4</sub><sup>2-</sup> was found to be the chemical interaction with Ca<sup>2+</sup>, which entered the brick from the poultice in the anode chamber. The concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in the pore solution decreased after 5 days of ED and precipitation of gypsum was thus not considered as a permanent problem. Simulation results were congruent with those obtained experimentally. The present experimental work (Fig. 4) support this conclusion, however, in case calcium-sulfate salt with low solubility is formed during ED, it will not necessarily be seen in the concentration profiles of figure 4, because the concentrations shown here are measured in a suspension of powdered sandstone in water after filtration. The salt crystals will be removed from the sample during the filtration process if not dissolved. Thus it is necessary

to evaluate the ED process also on the decay pattern, which was done by suction cycles, see section 3.3 of this paper.

Electro neutrality is fulfilled all the time and thus during ED other anions than  $\text{SO}_4^{2-}$  ensures the electro neutrality in relation to the  $\text{Na}^+$  concentration profile, as the concentration of this cation is high close to the cathode where the  $\text{SO}_4^{2-}$  concentration is low. In Paz-Garcia *et al.* (2013) it is suggested from numerical-chemical simulations that these are mainly  $\text{OH}^-$  ions (experimentally it is also often seen that *pH* increases slightly from the cathode side, which was also the case in the present work see section 3.4). There may thus be precipitation of  $\text{Ca}(\text{OH})_2$  in the material if  $\text{Ca}^{2+}$  from the anode poultice and  $\text{OH}^-$  from the cathode meet inside the stone. Over time  $\text{Ca}(\text{OH})_2$  may react with  $\text{CO}_2$  from air and form  $\text{CaCO}_3$ , but neither  $\text{Ca}(\text{OH})_2$  nor  $\text{CaCO}_3$  are considered damaging, because aqueous solutions of calcium hydroxide (limewater) have been used for many centuries to protect and consolidate limestone, and  $\text{CaCO}_3$  is present in the original carbonaceous stone.

### 3.3. Decay of ED treated stone evaluated after suction cycles

Pictures of the stones Ref and ED's after two cycles of water suction are shown in Fig. 5. Some of the thin white layer on the upper horizontal surface originates from the poultice (see also Fig. 3). During the suction, the soluble salts are transported towards the top of the stone, which means a concentration of salt in this part and a lower concentration in the remaining stone. It is seen that the upper corners were damaged for the Ref and ED<sub>2</sub> experiments whereas similar damage was not seen for ED<sub>4</sub> and ED<sub>7</sub> revealing that the overall concentration was lowered sufficiently after 4 days.

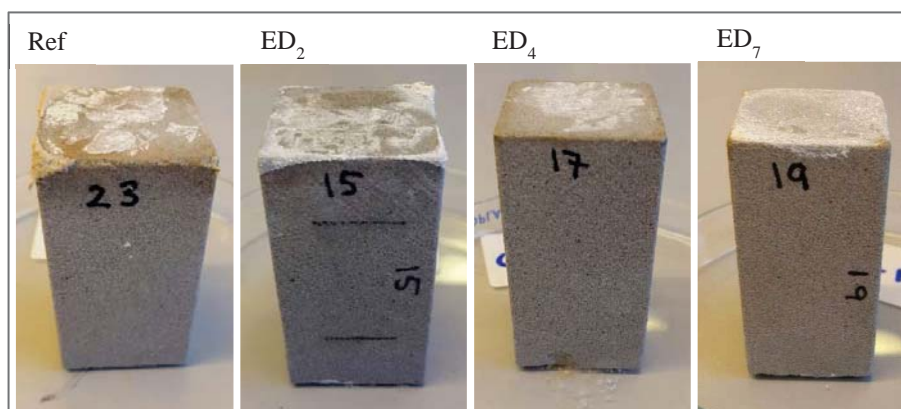


Fig. 5: Ref and ED stones after two water suction cycles.

It is noticed, that the soft material/crystals at the damaged corners of the Ref and ED<sub>2</sub> stone differs. At the Ref. it has the colour of the sandstone and at ED<sub>2</sub> the salt crystals are white. It might be different salts responsible to the decay in the two cases, but it is not determined in this investigation. In the Ref stone the  $\text{Na}_2\text{SO}_4$  in which the stone was submerged is considered the major salt, whereas in ED<sub>2</sub> also  $\text{Ca}^{2+}$  may have been transported from the anode poultice into the stone. The calcium sulphate will dissolve again as long as  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are removed from the pore solution in the applied electric field as equilibrium supports the dissolution. The lack of crystals on ED<sub>4</sub> and ED<sub>7</sub> support this hypothesis.

### 3.4. Compressive strength of ED treated stone

The average  $pH$  in the segments from Ref. was  $8.9 \pm 0.05$  and for ED<sub>7</sub>  $9.0 \pm 0.3$ . The overall  $pH$  in the stone piece did thus not change significantly during ED. The  $pH$  remained the same in the anode end as initially, whereas the  $pH$  increase from the cathode was not buffered to the same extent, as  $pH$  in the segment closest to the cathode was increased to 9.5, which is though not considered a problematic level.

The fact that the  $pH$  did not change from the anode side is not a proof that  $H^+$  did not electromigrate into the stone. Gotlandic sandstone has a buffering capacity towards acid as it is calcite bound, which was shown experimentally in Skibsted (2014). In case an acidification had occurred during the ED treatment, this would decrease the compressive strength of the stone as result of dissolution of calcite. Thus it was decided to make compressive test measurements. The compressive strength tests were conducted after the suction cycles, and the stone compressive strength could be influenced from both acidification and salt weathering. The result is shown in fig. 6 and 7. A quite large variation in compressive strength was observable between the four stones. The Ref. stone had the lowest compressive strength of all four stones, which may indicate that ED does not lower the strength significantly by dissolving the bonding calcite phases, but the data are too scarce to make a final conclusion on this point. Fig. 7 shows that the pattern with which the stones were broken during the compressive strength tests differed. The pattern was linked to the compressive strength in that for the Ref and ED<sub>7</sub> stones with the lowest compressive strength, the stones were damaged by flaking from the surface, whereas the two stronger stones ED<sub>2</sub> and ED<sub>4</sub> were broken in the expected pattern hourglass figure for a homogeneous sample.

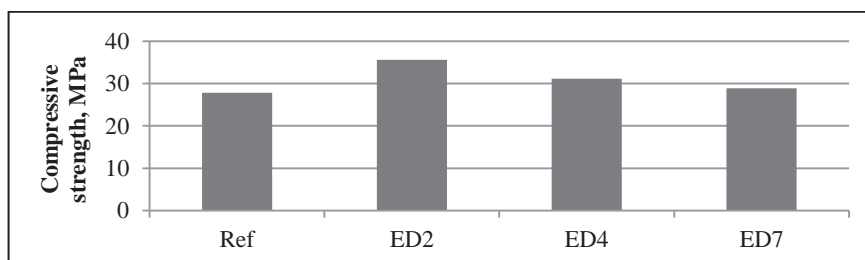


Fig. 6: compressive strength after ED and 2 suction cycles (single determinations).



Fig. 7: The stones after compressive strength measurements.



#### 4. Conclusions

Carbonate bound sandstones are weak and sodium-sulphate a highly damaging salt. ED was tested for removal of sodium-sulphate from Gotlandic sandstone, which is carbonate bound. The focus was on possible damaging side effects, such as dissolution of the carbonate phase or formation of new damaging salts, during the treatment. No indications of these side effects were seen. The compressive strength of the stones were measured and it was not decreased during ED, though this determination was only made in single determinations and the result must be taken with caution. The ED treatment followed by suction cycles did not show any stone damage after ED during 4 days, which was on the contrary to before treatment.

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