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# Salt Weathering on Buildings and Stone Sculptures

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# Electrochemical desalination of the ionic mixture measured in the vault of Rørby Church– Laboratory scale

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## ABSTRACT

*Salt induced deterioration of the vault in Rørby Church has resulted in extensive deterioration of the vault itself and of the murals on the lower surface of the vault. The upper surface of the vault has previously been covered with cement mortar. After removing this cement mortar some of the bricks erode and form brick powder. The brick powder was collected in 2002, 2005 and 2011 and measured for the most common salts in Danish vault structures. On the basis of the actual measured ions two different salt mixtures were made and used for contamination of brick specimens. By use of an applied electric DC field the nitrate and chloride contents were reduced to very low contents and the sulphate content was significantly reduced in the main part of the specimens. According to the results of the experiments it seems likely that the present ions in the upper part of the vault of Rørby church can be extracted electrochemically if the salts in the construction can be dissolved.*

Keywords: ionic mixture, church vault, electromigration, desalination

## 1 INTRODUCTION

A Danish investigation of 330 churches identified 33 churches suffering from salt induced deterioration (Trampedach 2008). One of these was Rørby Church located near the west coast of Zealand around 100 km from Copenhagen. The church was founded in the 12<sup>th</sup> century and rebuilt in the late medieval times. At the beginning of the 15<sup>th</sup> century two brick vaults were built in the west end of the nave and soon after decorated with some of the finest murals in Scandinavia from this period. The murals were executed on a support of lime plaster and two layers of lime wash. The colours were applied in a mixed lime painting technique using yellow and red earth pigments, minium, lead tin yellow and copper chloride. For the finale outlining and the text bands the painter used powdered charcoal (Bøllingtoft 1985). After the Reformation during the middle of the 16<sup>th</sup> century the paintings were covered with lime wash.

Because of erosion of the upper surface of the vault it was covered with a cement mortar around 1900. In 1980 -1982 the murals in one of the vaults were uncovered by the National Museum of Denmark. Because of a large amount of rain water penetrating the vaults in 1981 and 1999 the murals were heavily deteriorated by salt coming from the bricks (Bøllingtoft & Larsen 2003).



Figure 1. Bricks left uncovered, the area from which the brick powder was collected. Foto: The National Museum of Denmark, 2001.

In 1999 a part of the cement mortar was removed from the upper side of the vault leaving one quarter of the bricks uncovered. This show that a large part of the bricks had been eroded to up to 25% of their original thickness.

Brick powder collected with a brush from the same area (figure 1) in 2002, 2005 and 2011 shows a constantly ongoing deterioration of the bricks.

One method to extract the damaging salts is by use of an electrochemical method. Previously, electrochemical extraction of the common single salt sodium chloride has been carried out with high efficiency and to very low contents (Rörig-Dalgaard 2009). Also experiments with other single salts: potassium chloride and nitralite have been carried out (Ottosen & Rörig-Dalgaard 2009; Ottosen & Rörig-Dalgaard 2008). However, according to an investigation of around 1000 samples from Belgium, only in 13 % of the samples the number of anions was restricted to one (De Clercq 2005). Related to Danish churches the most typical salts are Na, Ca, Cl, NO<sub>3</sub>. Additional also SO<sub>4</sub> and CO<sub>3</sub> can be found as in the case of Brarup and Rørby Church (Larsen 1999). Electrochemical salt extraction has been carried out on a pilot scale with salt mixtures (e.g. (Ottosen et al. 2008), however laboratory experiments clarifying processes during the treatment have not been carried out to the authors knowledge.

In the present work powder originating from the decomposed bricks above the vault of Rørby Church has been collected, and the actual ionic contents were measured and chosen as representative values for salt mixtures for electrochemical desalination experiments.

## 2 MASS AND MEASURED IONS IN THE BRICK POWDER COLLECTED ABOVE THE VAULT OF RØRBY CHURCH

In April 1998 the cement mortar was removed from the top of the vault in Rørby church. On the 16<sup>th</sup> of October 2002 decomposed brick powder was collected with a brush, again on the 8<sup>th</sup> of February 2005 and most recently on the 25<sup>th</sup> of February 2011 from the same area and shown in figure 1, see table 1. The collected brick powder is from an area consisting of both brick and lime mortar joints. The joints account for 20-25% of the total surface area. In table 1 a continuously, however decreasing mass of deteriorated brick powder above the vault has been collected within the last almost 10 years.

Table 1. Decomposed brick powder collected from the top of the vault in Rørby church.

Weight of collected deteriorated brick powder	Mass pr m <sup>2</sup> [g/m <sup>2</sup> ]	Mass per m <sup>2</sup> pr year [g/(m <sup>2</sup> ·year)]
2002 after 4 ½ years	2185	486
2005 after 2 ½ years	699	280
2011 after additional 6 years	1236	206

The ionic contents of Na, Ca, Cl, NO<sub>3</sub>, SO<sub>4</sub>, K and Mg were measured and shown in figure 2 as the average of the contents from 2002, 2005 and 2011 (triple determination from each year) both as wt% and mole/kg. K and Mg were only measured in the brick powder from 2011 (as triple determination).

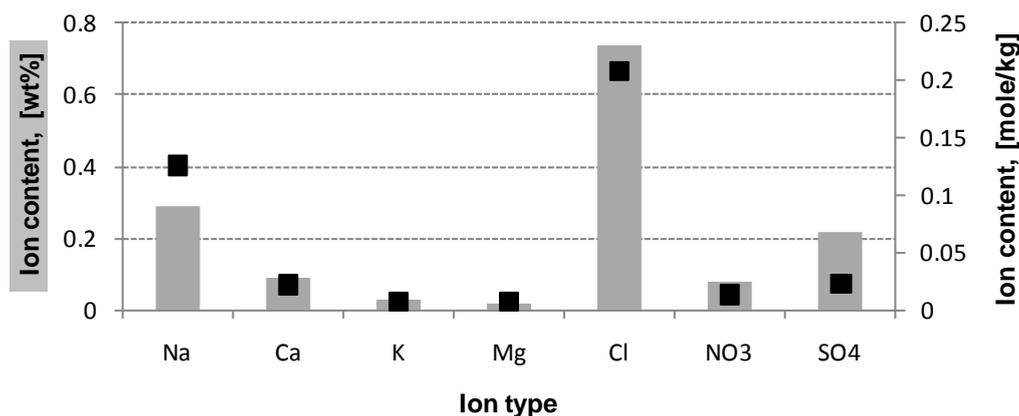


Figure 2. The ion contents in the decomposed brick material collected above the vault in Rørby church shown both as wt % (the gray bars and primary y-axis) and as mole/kg (the black squares and secondary y-axis).

Provided the average of the sodium content from 2002, 2005 and 2011 (0.126 mole/kg) is given the relative number 1, the relative numbers of Ca, K, Mg, Cl, NO<sub>3</sub> and SO<sub>4</sub> are as shown in table 2.

Table 2. Relative number of the present ions.

Sample material	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Brick powder, on average (2002+2005)	1	1/5	1/10	1/10	1 3/5	1/10	1/10

For the subsequent investigation it is aimed to reproduce these ratios. The measured calcium content must partly originate from the lime mortar; however this content is also included in the experiments with bricks to clarify the transport of calcium contaminated bricks in an applied electric field. In the solution there must be molar charge equilibrium. The calculated contents shown in table 2 outlines a relative number of negative charge of 1 7/10 and a relative number of positive charge of 2. This difference between the positive and negative charge is 3/10 (15%), however the relative numbers represents the majority of the species in the brick powder.

The measured ion contents in the brick powder (figure 2 and table 2) can be obtained in solution by adding (in ratios) the salts shown in table 3 and is in the following termed salt mixture 1. E.g. a relative number of 1/10 for both potassium and nitrate can be represented by 1/10 KNO<sub>3</sub>. The used salts must dissolve in solution and therefore the salt's solubility is taken into account. Therefore CaSO<sub>4</sub>·2H<sub>2</sub>O was added until maximum solubility (2.4 g/L according to (Larsen 1999)) and subsequently additional sulphate was added as MgSO<sub>4</sub>·7H<sub>2</sub>O. The used salts for salt mixture 1 are by (Arendt & Seele 2001) described as common building salts.

To investigate possible use of electrochemical desalination in case of other salt mixtures an additional salt mixture was prepared (salt mixture 2). On other church vaults in Denmark the highest cation content besides sodium has been measured for potassium (Larsen 1999) and a relative number of 1KCl was added to salt mixture 2 compared to salt mixture 1.

The present results from electrochemical desalination will be compared with previous results obtained by use of a solution solely contaminated with the single salt NaCl. In this previous investigation (Rørig-Dalgaard 2009 B), the total anion content was 1.0 wt% and the same type of bricks as in the present investigation was used. By taking the material properties of the bricks

into account, the anion content in the solution in which they were submerged was 1.36 mole/L. For reason of comparison the total amount of anions (and cations) in salt mixture 1 and 2 was chosen to 1.36 mole/L.

Table 3. Overview of the used solutions for contamination of the brick samples.

	The ratio of salts added to distilled water
Salt mixture 1	1 NaCl
	1/5 { CaSO <sub>4</sub> ·2 H <sub>2</sub> O (until max solubility of 2.4 g/L), MgSO <sub>4</sub> ·7H <sub>2</sub> O (the rest)
	1/10 KNO <sub>3</sub>
Salt mixture 2	1 NaCl
	1/5 { CaSO <sub>4</sub> ·2 H <sub>2</sub> O (until max solubility of 2.4 g/L), MgSO <sub>4</sub> ·7H <sub>2</sub> O (the rest)
	1/10 KNO <sub>3</sub>
Single salt solution	1 KCl
	NaCl

\*The experiments were carried out in a previous investigation (Rörig-Dalgaard 2009 B)

### 3 ELECTROCHEMICAL DESALINATION

When a salt as e.g. CaSO<sub>4</sub>·2H<sub>2</sub>O is brought into contact with water it dissolves into charged ions until the salts solubility has been reached. CaSO<sub>4</sub>·2H<sub>2</sub>O dissolves into Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. When positive and negative electrodes are established in the solution or in the pore system in a porous material, a current flow carried by the ions will proceed and the ions will be attracted towards the electrode of opposite sign. This phenomenon is termed electromigration which causes a controlled electrochemical transport of ions in porous moist materials like bricks

To establish an electrical circuit a transformation of the ions in the solution to electrons in the electrodes is necessary. These transformation reactions are termed electrode reactions and results in production of acid at the anode ( $\frac{1}{2} \text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}^+ + \frac{1}{4} \text{O}_2(\text{g}) + \text{e}^-$ ) and base at the cathode ( $\text{H}_2\text{O}(\text{aq}) + \text{e}^- \rightarrow \text{OH}^- + \frac{1}{2} \text{H}_2(\text{g})$ ). To avoid damaging pH changes, the electrode reactions can be buffered in an accumulating poultice (Rörig-Dalgaard 2009).

### 4 EXPERIMENTAL

#### 4.1 Sample selection, material and specimen preparation

The brick powder collected above the vault of Rørby Church was spread on a piece of paper in a line made of many thin curves made on top of each other. Three samples were taken straight forward perpendicular to the lines long side.

The brick was of the type Falkenløve red (handcrafted, fired in a circular kiln), with the saturation coefficient: 12.6 wt%, open porosity: 33.0 vol.-%, dry density: 1790 kgm<sup>3</sup>. The size of the brick specimen was 5 cm × 5 cm × 11 cm. The specimens were submerged into the two different solutions for 2 days. Subsequently the specimens were carefully wrapped in plastic film to minimize evaporation during the experiments.

#### 4.2 Setup and sampling positions

The setup consists from the left to the right of: the anode, accumulating poultice (consisting of kaolin clay, calcium carbonate and distilled water buffering the produced  $H^+$  at the anode), brick, accumulating poultice (consisting of kaolin clay and acidic acid buffering the produced  $OH^-$  at the cathode) and cathode. A constant current of 20 mA was applied across the setup.

The numbers indicate the sampling positions: 1.8 cm; 3.7 cm; 5.5 cm; 7.3 cm and 9.2 cm from the left of the brick, where left is the end next to the anode. The samples were extracted with a drill from the top through the brick specimens.



Figure 2. The experimental setup and indication of the sampling positions (the numbers).

#### 4.3 Analytical

Simple extractions in distilled water were made to evaluate concentration of the ions. The drilling samples were dried at  $105^{\circ}C$  until equilibrium (one day). The extractions were made with the drilling powder from each position (around 2-5 g) and 12.5 mL distilled water. The suspensions were agitated for 24 hours. Afterwards 2 mL of the suspension was added to a mixture of 40 mL distilled water and 1 mL 1M  $HNO_3$  (added as the standard row for measuring is related to  $HNO_3$ ). After filtration, the anion (sulphate, nitrate and chloride) concentrations were measured with ion chromatograph and the cation (calcium, sodium, potassium and magnesium) concentrations were measured with AAS (Atomic Absorption Spectroscopy).

### 5 RESULTS AND DISCUSSION

Two experimental series were initiated: one series with salt mixture 1 and one with salt mixture 2. Each series consisted of 5 experiments, one reference experiment without an applied electric DC field which for 14 days was placed next to the other experiments, and the remaining four experiments in each series with applied electric DC field for 4, 6, 14 and 21 days respectively. The results from the experiments are shown in figure 4. In figure 4a, 4b and 4d the results from the experiments with salt mixture 2 are outlined. Figure 4 c shows the sulphate results with salt mixture 1 and in figure 4e the chloride results from a previous experiment (Rørig-Dalgaard 2009 B) with a similar setup, same brick type and total molar anion concentration with the single salt sodium chloride is shown.

After application of an electric DC for 4 days across the experiments with salt mixture 2 the nitrate and chloride content was reduced significantly (figure 4a and figure 4d) compared to the reference experiment without applied electric DC field in position 4 and 5 meaning at least the 4 cm closest to the cathode (the negative electrode). After 6 days experimental duration, the

chloride and nitrate contents were reduced to 0.0048 +/-0.0013 wt% for chloride and 0.0002 +/-0.0004 wt% for nitrate throughout the whole brick. The results from the series with salt mixture

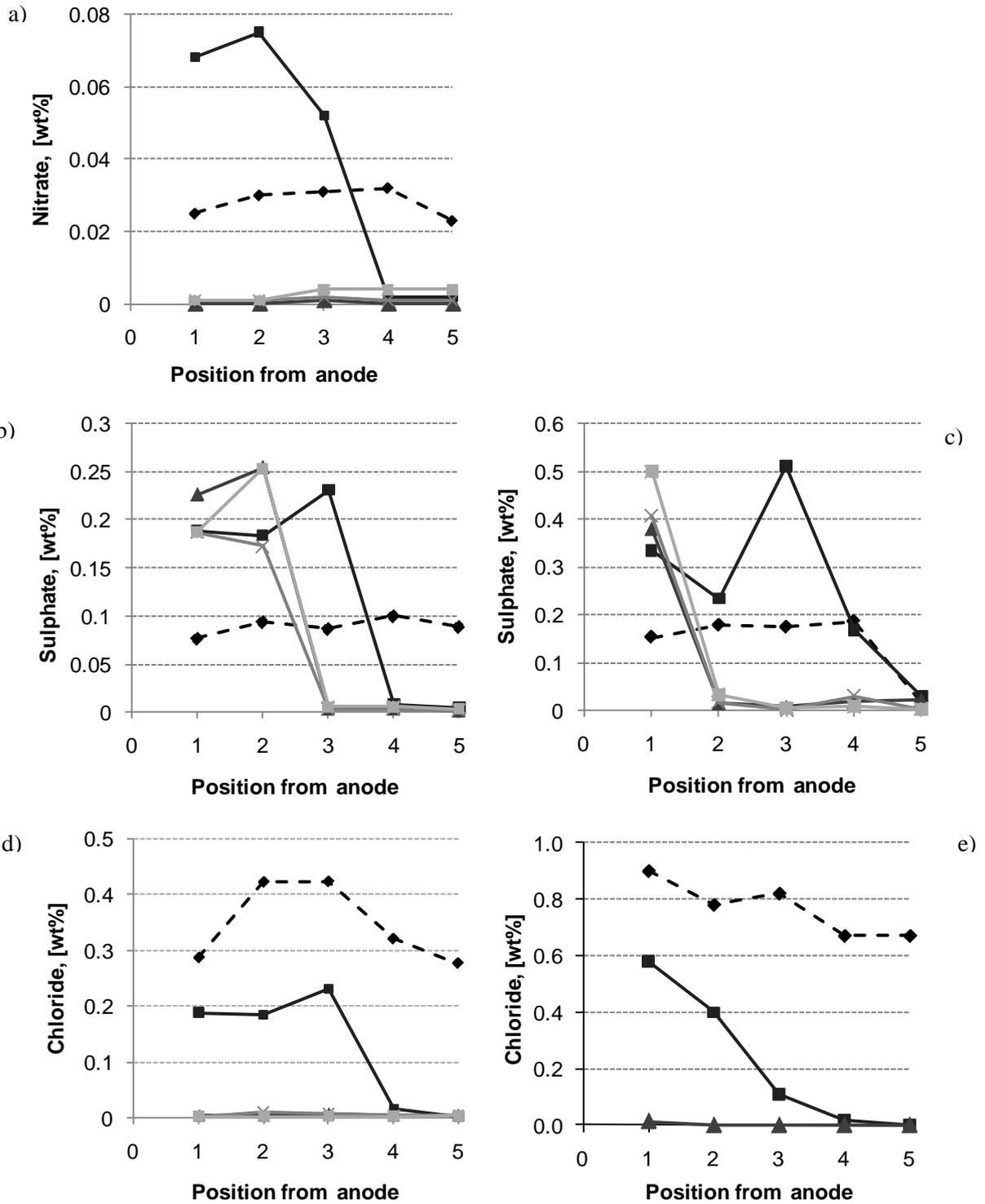


Figure 4. Development in the anion contents. ♦ reference (14 days without applied electric DC field), ■ 4 days, ▲ 6 days, × 14 days and ▣ 21 days with applied electric DC field shown for: a) nitrate (salt mixture 2), b) sulphate (salt mixture 2) c) sulphate from salt mixture 1, d) chloride (salt mixture 2) and e) chloride (the single salt sodium chloride, (Rörig-Dalgaard 2009 B)).

1 showed the same tendencies (not shown). A reduction to low contents of both nitrate and chloride therefore seems uncomplicated also when they are a part of a salt mixture.

In figure 4b the results from the experiments with salt mixture 2 are shown. After 4 days significant reduction in the sulphate content had occurred in position 5 (around 2 cm from the right end towards the cathode). An additional reduction occurs between 6 and 14 days, however between 14 and 21 days no further reduction was measured. The same pattern for transport of sulphate in the bricks contaminated with salt mixture 1 is seen in figure 4c. However, a higher removal was obtained after 6 days, compared with figure 4b meanwhile no significant additional reduction in the sulphate content was obtained between 6 and 21 days. This means that for both salt mixture 1 and 2, position 1 and in figure 4b, also position 2 still has high sulphate contents and indicates a general tendency. This might be caused by new formation of a heavy soluble salt, e.g. a sulfate salt ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), which precipitates and hinders further electrochemical transport.

In figure 4d the measured chloride contents for salt mixture 2 are shown and in figure 4e the results from a previous investigation (Rørig-Dalgaard 2009 B) with the same setup, however with a salt solution consisting of the single sodium chloride are shown. By comparison of figure 4d with figure 4e it was possible to test the electrokinetic efficiency on the present mixture against the efficiency for a single salt, since the total amount of anions were the same in these two experimental series. In both cases the chloride content was in both cases reduced significantly after 4 days and was almost removed after 6 days. This suggests that presence of additional anions (and cations) do not change the efficiency of the electrochemical transport of chloride significantly. As the experiments were carried out as one off experiments, in 2 series with comparable results general tendencies was shown.

The used salt mixtures were determined on the basis of the collected brick powder above the vault and do therefore represent the precipitated salts and not necessarily the ions within the brick vault construction.

The present experiments were carried out with saturated brick species without drying and all salts were dissolved and thereby possible to transport in an applied electric field. In a previous investigation of desalination of a wall section by use of climate control to ensure a relative humidity above the salts' deliquescence point and application of an electric DC field, high salt removal efficiency was documented (Rørig-Dalgaard 2009 C). Therefore to carry out electrochemical removal of salt mixtures on a church vault construction the salt mixtures deliquescence point should be estimated to determinate the experimental conditions.

## 6 CONCLUSION

Continuous salt induced deterioration above the vault in Rørby Church documented through collected deteriorated material from the upper surface three times during the last almost ten years points out the need for action.

On the basis of the actual ion contents in the collected material from Rørby Church two different salt mixtures were made and used for contamination of brick specimens. Subsequently electrochemical desalination was carried out by application of an electric DC field across the brick specimens. The results showed a reduction of the chloride and nitrate to very low contents. The sulphate content was also significantly reduced in the main area of the specimens. Comparison with a previous investigation showed similar electrochemical desalination efficiencies for bricks contaminated with a single salt and salt mixtures.

By ensuring a relative humidity above the deliquescence point of the salt mixture it seems likely that the present ions in the upper part of the vault of Rørby Church can be removed electrochemically.

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## REFERENCES

- ARENDDT, C., SEELE, J., 2001. *Feuchte und Salze in Gebäuden*. Verlagsanstalt Alexander Koch GmbH Leinfelden-Echterdingen. 15.
- BØLLINGTOFT, P., 1985. *Den dømmende Kristus*. In Danske kalkmalerier, Gotik. Det Danske Nationalmuseum 1985, Article 18.
- BØLLINGTOFT, P., LARSEN, P.K. The use of passive climate control to prevent salt decay in Danish Churches. In *Mauersalze und Architekturoberflächen*. Hochschule für Bildende Künste, Dresden 2003, p. 90-93.
- DE CLERCQ, H., 2005. Performance of single materials treated with a water repellent and contaminated with a salt mix. In: Proceedings "4 th. International Conference on Water Repellent treatment of Building Materials", April 12.-13., 2005, Stockholm, Sweden, 171-184.
- LARSEN, P.K., 1999. *Desalination of painted brick vaults*. Thesis (PhD). Technical University of Denmark.
- OTTOSEN, L.M., RÖRIG-DALGAARD, I, 2007. Electrokinetic removal of  $\text{Ca}(\text{NO}_3)_2$  from bricks to avoid salt-induced decay, *Electrochimica Acta*, 52(10), 3454-3463.
- OTTOSEN, L.M., RÖRIG-DALGAARD, I, VILLUMSEN, A., 2008. Electrochemical removal of salts from masonry – Experiences from pilot scale. In: *Salt Weathering on Buildings and Stone Sculptures*. 22-24 October 2008 Copenhagen, Denmark, 341-350.
- OTTOSEN, L.M., RÖRIG-DALGAARD, I, 2009. Desalination of bricks by application of electric DC field, *Materials and Structures*, 42(7), 961-971.
- RÖRIG-DALGAARD, I., 2009. *Preservation of murals with electrokinetic – with focus on desalination of single bricks*. Thesis (PhD). Technical University of Denmark.
- RÖRIG-DALGAARD, I., 2009 B. Chloride transport in masonry (brick and cement mortar) in isolated and combined systems. In: *The International Conference on Concrete Solutions*. 22-25 June 2009 Padua, Italy, 29-33.
- RÖRIG-DALGAARD, I., 2009 C. Desalination for preservation of murals by electromigration and regulated climate. In: *Structural Studies, Repairs and Maintenance of Heritage Architecture XI*. 22-24 July 2009 Tallinn, Estonia, 71-82.
- TRAMPEDACH, K. 2008: <http://kalkmaleriinfo.natmus.dk>