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FIRST EXPERIENCES WITH ELECTROCHEMICAL IN-SITU DESALINATION OF BRICKS IN A CHURCH VAULT CONSTRUCTION

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ABSTRACT

Deterioration of surfaces on building constructions and especially historical constructions caused by presence of salts is a well known problem in Europe and on other continents as well, however there is still a lack of an efficient desalination method. Salt induced deterioration is especially problematic in relation to church vault constructions with murals as the surface deterioration can result in loss of valuable cultural heritage. An electrochemical method has been investigated with focus on possible use for desalination of salt loaded vault constructions with murals in laboratory scale.
In the present paper all necessary considerations were made and described prior to electrochemical in-situ desalination. Experiences in getting started with experiments on cultural heritage has been obtained, it needs some extra time and should therefore be considered as an extra step during the preparation phase. Salt profiles were made from three different positions in one brick in the church vault construction in Rørby church and satisfying concordance was found between these salt profiles. An area without any original plaster and murals favourable for the construction of a small climate chamber was chosen. Salt profiles from three different bricks within this area clarified two bricks with low ion contents and one with a high ion content which is representative for church vault constructions. The idea of using a climate chamber for dissolution of present salts for minimizing additional water supply during the desalination was theoretically supported and at present only the permission to initiate the electrochemical in-situ desalination is missing.

Keywords: *Electrochemical desalination, In-situ, Church vault construction, Clay bricks*

1. INTRODUCTION

Salt induced deterioration is generally recognized as a frequent cause for deterioration of structures. In cause of new buildings salt induced deterioration is related to increased maintenance and thereby related costs. However, in relation to cultural heritage salt induced deterioration is a serious threat against future existence.
Previous used desalination methods were in practice shown to be limited effective [1]. Recently developments of the compress method have resulted in increased efficiencies by adjusting the pore size distribution of the poultice to the specific material to be desalinated and efficiencies between 50 and 90 % has in general been obtained by taking the pore size distribution into account [2]. According to [3] there is no single ideal poulticing method for extracting salts at present, and that in practice one can never achieve complete desalination of a non moveable object. The compress method has also recently been studied by MNR to clarify the water and salt transport non-destructively [4].
An alternative method for desalination, electrokinetic desalination, has up till now been subject for:

1) Optimization of the desalination effect [5, 6].
2) Desalination of single bricks [5, 7].
3) Investigation of the effect on different materials (bricks, different mortar types) [8, 9].
4) Investigation of the desalination effect in case of different salts [10].
5) Desalination of a wall section and optimization of this [11, 12].

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All these investigations have been carried out by taking the conditions in churches and church vault constructions into account with the aim to develop the method for this specific purpose.
However, the crucial point is whether the promising results during all these laboratory investigations can be transferred to electrochemical desalination of bricks in a church vault construction.
The idea with the present work is to combine the use of regulated climate (for dissolution of the present salts) and an applied electric DC field to minimize the demand for additional wetting and hence problems connected with the wetting. Wetting of historical structures for desalination can result in a negative impact on water sensitive materials as e.g. binders and pigments [13]. Too much water implies the risk that salts get transported deeper in the substrate [2] and at RH above 65% microbial activity and thereby microbial deterioration have been found [14].
The present paper deals with the first experiences with electrochemical in situ desalination of bricks in a church vault construction including the procedure for obtaining permission to carry out the desalination with this new method and determination of the consistence between salt profiles in three different positions in the same brick.

2. BEFORE GETTING STARTED

Working with cultural heritage in situ requires additional preparation compared to traditional historical masonry as in [15]. After preparation of the setup for the experiment in the autumn of 2011, the supervisory authorities pointed out the need to write an application for the diocese. The diocese would then ask the local parochial church council for permission which advised by the National Danish Museum will make their decision. This process is still ongoing.

3. THE VARIATION OF THE SALT CONTENT IN THE CONSTRUCTION

For the previous laboratory experiments, the bricks were submerged in a saline solution to obtain an equal distribution of the added salt throughout the brick. Contrary, the in situ experiments will be carried out on bricks with the present salt contents. Therefore drilling samples were extracted from the church vault to determine the present salt content. Initially samples were extracted in three positions from the same brick throughout the total depth of the brick to clarify the consistence of the measurements. The chosen brick is situated below the vault and was selected as it is a visual deteriorated brick and limited original material would be affected by the investigation. See (Fig. 1).

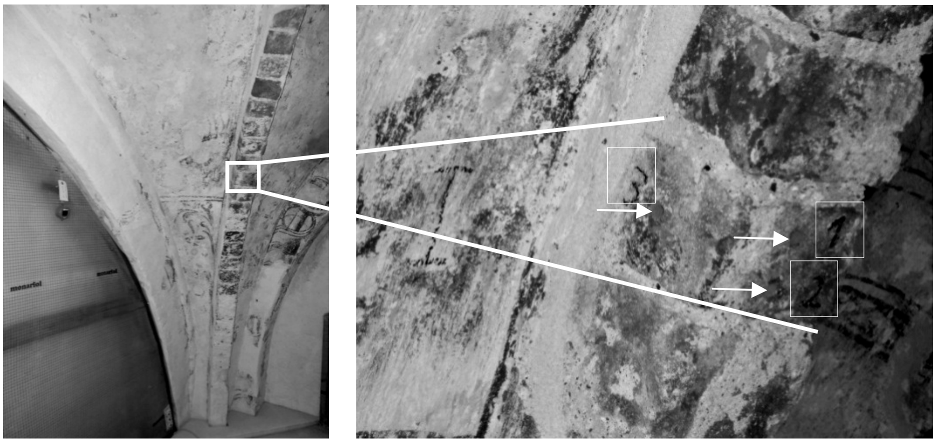

Fig. 1 An overview is shown to the left where the selected brick "I" is marked with a white box. A close-up is shown to the right where the three positions "I1", "I2" and "I3" is made clear with an arrow. Foto: Inge Rörig-Dalgaard

4. TRANSPORT OF WATER AND IONS IN SATURATED MATERIALS

Moisture transport in porous materials can proceed as vapour diffusion, surface diffusion and capillary flow and each of the three processes proceeds with increasing moisture content. Salts in shape of dissolved ions cannot be transported during vapour diffusion as a continuous water layer is not present. Contrary, in the hygroscopic region at high relative humidity's, surface diffusion including a continuous water layer can take place increasing with rising relative humidity where the driving potential is differences in relative humidity´s [16]. The surface diffusion (w_s, [kg/ m s]) is defined as:

$$w_s = \delta\left(\frac{1}{\mu(\varphi)} - \frac{1}{\mu_0}\right) p_{sat} \cdot \frac{d\varphi}{dx}$$

where: δ = water vapour conductivity in air [kg/m s Pa], $\mu(\varphi)$ = water vapour resistace in "wet" material (relative to air) [–], μ_0 = water vapour resistance in dry material (relative to air) [–], p_{sat} = saturation vapour pressure [Pa], φ = relative humidity [–].

5. THE PRINCIPLES OF ELECTROKINETIC DESALINATION

Electric current represents a systematic movement of electrically charged particles and can occur in both a liquid (electrolytic charge) and in metal (metallic charge). By connecting the movement of charged particles in a liquid and in two metallic electrodes, a circuit is established (termed an electrochemical cell). This transport of current inside the electrical circuit can be initiated by use of an power supply and can be termed an electrolytic cell (defined by the surroundings can perform electrical work on the cell) [17]. This transport of charged particles can be utilized to transport of ions (dissolved salt) in constructions towards its surfaces from were they can be removed. Negatively charged ions (anions) are attracted towards the positive charged electrode (anode) and the positively charged ions (cations) are attracted towards the negatively charged electrode (cathode).

For this to come into existence sufficient water must be present to dissolve the present salts. In addition special attention must be taken to the electrode material as it in some cases will decompose and to the adverse effects related to the reactions transforming the ions into electrons and following the electrons into ions (termed electrode reactions). This problem was dealt with in previous work and is left out here see, e.g. [5]. Additionally, operational conditions and practical setup has been documented to determine the desalination efficiencies [5-12, 15].

6. EXPERIMENTAL PREPARATION AND CONDITIONS

6.1. Selection of the bricks to be desalinated and their preparation

An area without any murals or original mortar at the lower surface of the vault and with the possibility relatively simple to erect a climate chamber above the area was selected. To find the best area, a presumed area was identified and the accurate bricks were pointed out at the upper side of the vault by making a drill in a joint from below the vault up through the vault construction. Several possibilities were considered in relation to the establishment of a small climate chamber above the vault. An area in the easthern part of the vault facing north was chosen. From this area three medieval bricks will be taken out from the church vault construction by use of an electrical cuting tool, see the marked area in (Fig. 2).

Fig. 2 The selected area for the in-situ desalination of the bricks (a), (b) and (c) is marked with the white line. Foto: Nordic Conservation 2011

The extraction is carried out by an experienced conservator from Nordic Conservation which will pay special attention to the original bricks and only the mortar joints will be influenced by the intervention. All three mediaval bricks will be cleaned off for mortar from the joints, measured up and are to be foto documented before replacement of the bricks (b) and (c) in the vault. The third brick (a) is replaced by a new brick made for restoration purpose with a well-known salt content and is placed in construction together with the two other bricks. Brick (a) serves as a referece and for comparison with previous electrochemical desalination in laboratory scale with this specific brick type (handmade, fired in a circular kiln, produced by Falkenløwe).

The replacement of the medival bricks and the new brick will be carried out with limemortar (1 part lime putty to 3 parts sand (0-2 mm) to ½ part crushed lime stone (from 0-40 micron)) and special developed shims (not described here). The bricks are prior to this action wrapped in laboratory film with the purpose subsequently to be able to measure the electrokinetic desalination effect on each of the bricks. This proceedure will prevent any ions during the desalination to dissapear sideways and thereby interfere with the measurement results. Contrary it can be argued that sideway transport of ions is one of the usual problems in relation to in-situ desalination which should be solved as a part of the desalination treatment.

Electrodes for initiation of the electrochemical ion transport will solely be placed at the upper side of the vault. The electrodes will be fixed with a salt accumulating layer as in many previous laboratory experiments to avoid direct contact with the lower surface which in other cases could be covered by salt damaged and thereby fragile murals.

6.2. Establishment of a climate chamber

To minimize the nessessary applied water amount during the electrochemical desalination only a relative humidity above the salts deliquence point to ensure dissolution of the present salts to ions was desired. For this purpose the climate above and below the vault will be controlled by constucting a small climate chamber above the upper surface of the test area in addition to the climate chamber which has been present below the vault for several years. Since the chosen bricks in the test area are to be isolated from the surrounding bricks only insurance of a specific climate exactly above the test area will be necessary.

6.3. Electrochemical desalination and concluding conditions

The electrokinetic threatment is expected to be ongoing for 3-12 weeks dependent on the specific ion content in the bricks and dependent on the actual obtained desalination efficiancy in-situ. After the desalination the effect will be evaluated by taking 8 mm wide drilling profiles from each brick to compare with the results found prior to the electrochemical desalination.

After ended electrochemical desalination the bricks will be removed again, the laboratory film (produced by pechiney plastic packaging) removed and the three medival bricks re-set in the vault construction with lime mortar. The practical work in connection with the in-situ desalination will be carried out by Nordic Conservation and in consultation with the church consultances from the national museum.

7. RESULTS

7.1. Coincidence of the salt profiles in three different positions in the same brick

The measured contents of chloride, nitrate and sulphate in positions I1, I2 and I3 are shown in (Fig. 3), (Fig. 4) and (Fig. 5).

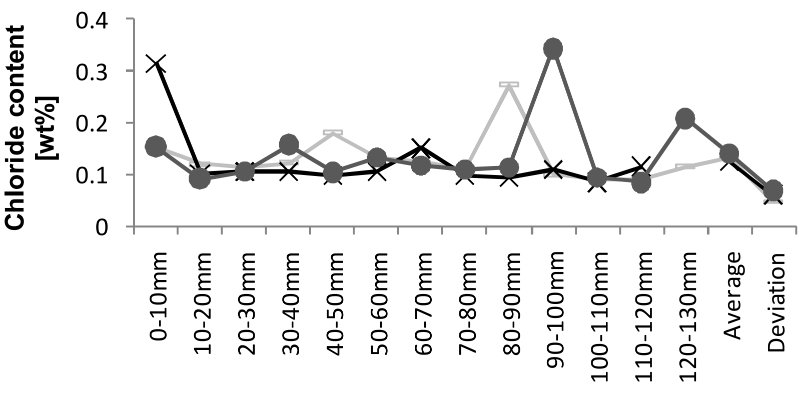

Fig. 3 The chloride content in three different positions –: I1, ×: I2, ●: I3 in the same brick as a function of the depth

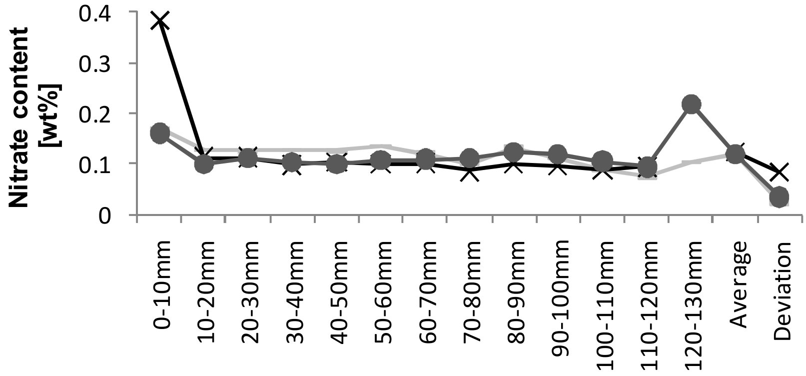

Fig. 4 The nitrate content in three different positions –: I1, ×: I2, ●: I3 in the same brick as a function of the depth.

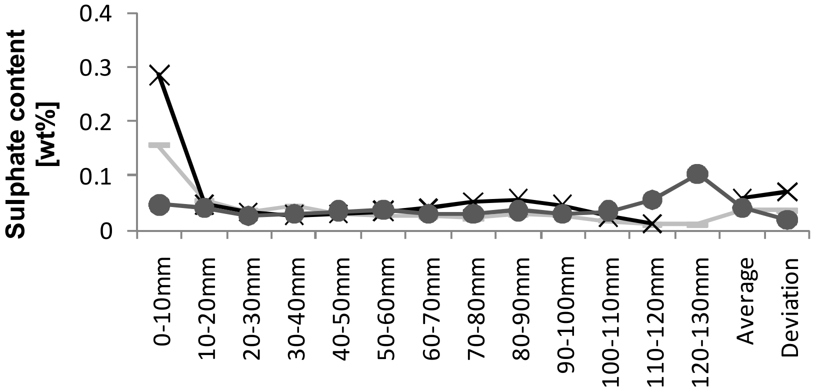

Fig. 5 The sulphate content in three different positions -: I1, ×: I2, ●: I3 in the same brick as a function of the depth

7.2. The ion content in the bricks to be desalinated

The ion contents in brick a, b and c was determined for each 10 mm and their average values throughout the whole bricks depth are shown in (Tab. 1).

Table 1 The average chloride, nitrate and sulphate content in the bricks a, b and c

Brick	**Chloride** [wt%]	**Nitrate** [wt%]	**Sulphate** [wt%]
A (ca 120 mm in depth)	0.04 +/- 0.01	0.00 +/- 0.00	0.01 +/- 0.01
B (ca 130 mm in depth)	0.07 +/- 0.01	0.00 +/- 0.00	0.02 +/- 0.02
C (ca 80 mm in depth)	0.65 +/- 0.09	0.07 +/- 0.01	0.01 +/- 0.00

8. DISCUSSION

8.1. Coincidence of the salt profiles in the three different positions

Taking the deviation into account (0.5-0.7 wt %) similar ion contents were measured in the depths 10-120 mm for chloride except for 80-90 mm in position I1 and 90-100 mm in position I3. In the area closest to the surface (0-10 mm) significant higher chloride content was measured in position 2 than in 1 and 3 this is most probably caused by an accumulation of precipitated salts.

Except from the 10 mm closest to the inner surface and 10 mm closest to the upper side of the vault facing the roof, the measured nitrate contents in all three positions are similar (Fig. 4). The higher nitrate contents in the depth of 0-10 mm and 120-130 mm are thought to be caused by precipitation close to the surfaces.

The sulphate content (Fig. 5) was very similar in the depths 10-110 mm. In the depth 0-10 mm and 110-130 mm some deviation was found. In position I2, the brick was only 120 mm deep.

Addition of the average wt% of chloride, nitrate and sulphate in each of the three positions is 0.287, 0.303 and 0.300 respectively for I1, I2 and I3.

Regarding the chloride, nitrate and sulphate content in the positions I1, I2 and I3 there does not seems to be significant variations inside this brick. In [18] a typical salt profile of a cross section is evenly distributed throughout the whole profile in consistance with the present measured ion contents, however in the typical salt profile no increased ion contents were present close to the surfaces. Related to the chloride content minor variations in the exact position were measured. This could be caused by the fact that chloride salts has lower maximum deliquence points for traditional salts in structures than for carbonate, nitrate and sulphate [16] meaning the least water is necessary to transport ions originating from chloride salts which again means it is the first salt to be transported.

Since the total average wt % of chloride, nitrate and sulphate in each of the three positions is 0.287, 0.303 and 0.300 respectively for I1, I2 and I3 there seems to be a tendency for that even through some variation was measured between the positions 1, 2 and 3 the total ion content was almost the same in average. This suggests, that when the final ion content should be evaluated after ended experiment, also average values in total should be used and not only focusing on one specific measurement.

It is evident, that the RH inside the church would change during the week and during the year if there had not been a climate chamber. Above the vault no climate regulations have been carried out until now. Related to the actual ions, the ion mixtures ions will move inside the materials and salts will precipitate and dissolve at varying RH resulting in deterioration. In [16] it was shown that a change of 10% RH for just some few hours can result in phase transition, whereas smaller changes in RH for a longer period might not result in phase transition.

In [19] it was shown that the salt distribution of porous objects can vary considerably not only with location, but also in depth, and over time. The effect of this are particularly pronounced in the case of wall paintings and the factors “time” and “depth” may have to be build into the sampling strategy as well as “location”. Also, by taking replicate samples the degree of error within the data can be estimated which also allows application of statistical techniques. An approach to in-situ investigations that includes sampling and analysis with condition recording, and environmental monitoring enhances the usefulness of the information obtained greatly [19]. In praxis the changes in RH might result in the actual positions of the ions are changing, and comparison with drilling samples from another time period with different climatic environmental could be argued to be limiting describing. However, some reference measurements are needed and for this purpose the present measured values are satisfying.

8.2. The ion content in the bricks to be desalinated

In brick (a) the ion content is low and within the same level througout the total depth of around 120 mm for both chloride, nitrate and sulphate.

In brick (b) the chloride and nitrate content is evenly distributed throughout the total depth of around 130 mm, whereas the sulphate content increases in the upper 1/3 of the vault facing the roof. Both the chloride, nitrate and sulphate contents are low in brick (b) as in brick (a).

Brick (c) is visible deteriorated and only around 80 mm in depth. The average anion content is 0.73 wt%. Cf experience figures salt contents below 0.5 wt % will not result in salt induced deteriorarion, contrary to salt contents above 0.5 wt % [20]. Since solely the chloride content is above 0.5 wt% in all depths (ion profiles are not shown) it is likely that the visiable deterioration is caused by the salts.

The presence of salt contaminated bricks as brick (c) just next to bricks with a low salt contents as in brick (a) and (b) is not unusual and was among other recorded in Kirkerup Church in Denmark [16] and is one of the problems to be dealt with during desalination.

Since electrochemical desalination is dependent of the conductivity and thereby reverce dependent of the resistance the ion transport will naturally proceed were the lowest resistance is present and leave out areas higher resistance. Therefore varying salt contents can relative easely be taken into account and use of electrochemical desalination is therefore though to be anvantageous in relation to a construction with varying ion contents. Provided permission is given to carry out electrokinetic desalination on the three bricks in the vault of Rørby church (answer was expected in the end of March 2012 but was still not received medio april) the experiments are expected to be finalized medio 2012 and results will subsequently be presented. Afterwards the treatment will be evaluated together with the Danish National church consultancies’ regarding effects and eventual side effects resulting in whether additional electrochemical in-situ desalination can be carried out or whether additional optimization of the method has to be made before further use of the method in-situ.

9. CONCLUSIONS

Extensive preparation and considerations have been made beforehand to the electrochemical desalination both in the present paper and in previous work with the aim to remove the damaging salts from church vault constructions with murals for future preservation of these murals. Possible use of climate chambers to dissolve present salts for minimizing additional water supply during desalination has been theoretically founded; considerations have been made in relations to establishment of a climate chamber and to evaluation of the effect.

There was found consistence in the ion content in three different positions in the same brick which ease evaluation of the effect after future desalination. It was found that the ion content in two of the bricks to be desalinated already was very low, whereas the ion content in the last brick was high and damaging. This combination of non salt contaminated bricks and salt contaminated bricks just next to each other is usual in church vault constructions and therefore representative.

Series of laboratory experiments have been carried out in laboratory scale with conditions similar to existing conditions in church vault constructions make probable successful in-situ desalination.

Experiences with obtaining permission to carry out experiments on cultural heritage have been obtained and at present only this permission is missing before the electrochemical in-situ desalination can be carried out.

FUTURE WORK

From medio 2012 to 2014 the electrochemical method for preservation of murals will be investigated in a preservative manner. This project will be financed by the Augustinus Foundation.

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REFERENCES

[1] Brajer I., Larsen P.K. (2008) The salt reduction treatment on the wall paintings in Tirsted Church. In: *Proc. Salt Weathering on Buildings and Stone Sculptures* Copenhagen, Denmark, 219-228.

[2] Lubelli B., van Hees R.P.J., De Clercq H. (2011), Fine tuning of desalination poultices: try-outs in practice. In: *Proc Salt weathering on Buildings and Stone Sculptures* Limassol, Cyprus, 381-388.

[3] Pel L., Sawdy A. & Voronina V. (2010), Physical principles and efficiency of salt extraction by poulticing. *Journal of Cultural Heritage* 11: 59-67.

[4] Voronina V. (2011), *Salt extraction by poulticing: an NMR study*. PhD thesis. Technische Universiteit Eindhoven, The Nederlands.

[5] Rörig-Dalgaard I. (2009) *Preservation of murals with electrokinetic – with focus on desalination of single bricks*. PhD thesis. Technical University of Denmark.

[6] Rörig-Dalgaard I., Ottosen L.M. (2011), Method and device for removing an ionic impurity from building structures. EP 2 276 716 B1. Patent.

[7] Rörig-Dalgaard I., Ottosen L.M., Hansen K.K. (2012), Diffusion and electromigration in clay bricks influenced by differences in the pore system resulting from firing. *Journal of Construction and Building Materials* 27: 390-397.

[8] Rörig-Dalgaard I. (2009), Chloride transport in masonry (brick and cement mortar) in isolated and combined systems. In: *Concrete Solutions III* Padua, Italy, 29-33.

[9] Rörig-Dalgaard I. (2010), Electrochemical NaCl extraction from brick + lime mortar – Design of the used historical lime mortar. In: *8th Int. Masonry Conf.* Dresden, Germany, 375-382.

[10] Rörig-Dalgaard I., Bøllingtoft P. (2011), Electrochemical desalination of the ionic mixture measured in the vault of Rørby Church – Laboratory scale. In: *Salt weathering on Buildings and Stone Sculptures, SWBSS 2011* Limassol, Cyprus, 365-372.

[11] Rörig-Dalgaard I., Ottosen L.M., Christensen I.V. (2008), Desalination of a wall section with murals by electromigration. In: *Proc. Salt Weathering on Buildings and Stone Sculptures* Copenhagen, Denmark, 361-371.

[12] Rörig-Dalgaard I. (2009) Desalination for preservation of murals by electromigration and regulated climate. In: *Proc. 11th Int. Conf. on Structural Studies, Repairs and Maintenance of Heritage Architecture* Tallinn, Estonia, 71-82.
[13] Sawdy A., Heritage A., Pel L. (2008) A review of salt transport in porous media, assessment methods and salt reduction treatments. In: *Proc. Salt Weathering on Buildings and Stone Sculptures* Copenhagen, Denmark, 1-27.
[14] Petersen K. (1990) Mikroorganismen beschleunigen den Zerfall mittelalterlicher Wandgemälde. In Krumbein W.E. *Schäden an Wandmalereien und ihre Ursachen. Ein forschungsprojekt des BMFT Arbeitshefte zur Denkmalpflege 8.* 115-121.
[15] Ottosen L.M., Pedersen A.J., Rörig-Dalgaard I. (2007), Salt-related problems in brick masonry and electrokinetic removal of salts. *Journal of Building Appraisal* 3(3): 181-194.
[16] Larsen P.K. (1999) *Desalination of painted brick vaults*. PhD thesis. Technical University of Denmark. 28, 63-64.
[17] Hansen P.F. (2009) Electrochemistry. In Jensen O. M. (ed) *The science of Construction Materials.* Springer-Verlag, Berlin Heidelberg .
[18] Auras M., Melissa G. (2002) Kompressenentsalzung – Wirkungsprinzip, Materialien, Anwendung, Fallbeispiele. Salze im historischen Natursteinmauerwerk. In: *IFS-Tagung 2002*. Institut für Steinkonservierung e.V. Bereicht Nr. 14.
[19] Sawdy A., Price C. (2005) Salt damage at Cleeve Abbey, England. Part II: seasonal variability of salt distribution and implications for sampling strategies. *Journal of Cultural Heritage* 6 (2005) 361-367.
[20] Larsen P.K. (2007) The salt decay of medieval bricks at a vault in Brarup Church, Denmark. *Journal of Environmental Geology* 52: 375-383.