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Electrokinetic desalination of glazed ceramic tiles – preliminary results

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SUMMARY: Electrokinetic desalination is a method where an applied electric DC field is the driving force for removal of salts. The method is under development for desalination of brick masonry and stone monuments. In the present paper, the method is suggested for extraction of salts from tile panels, as well. It is suggested to remove few tiles from the panel, place electrodes in the holes and desalinate the wall and mortar behind the tiles. It was shown experimentally, that electrokinetics can be used for desalination of the tiles (96% Cl removed in less than 6 days). The method might be a conservation method to salt damaged tile panels.

KEY-WORDS: Desalination, chloride, tile, electrokinetics, electrodes

INTRODUCTION

Ceramic tiles are an important part of Portuguese cultural heritage and are worldwide appreciated. Azulejo tiles decorate inner and outer walls of churches, gardens, private houses, railway stations and a series of other buildings. One of the problems affecting tile panels is the formation of salt crystals, leading to the deterioration of the tile. Salts can accumulate on the surface or under the glaze, leading to glaze lifting, fractures, efflorescence, scaling and granular disintegration.

The salts can derive from the materials used for laying the tiles or might have an external source, such as water migration followed by salt crystallisation when water evaporates. Conservation actions at present follow one of two approaches: either the tiles are removed from their support for ex-situ treatment before they are placed in the original position again or else treating tile panels in situ. Current practice for in situ treatment is to use poultice materials. These are wet adhesive pastes which are applied to the surface in order to draw out soluble salts. Although poulticing is a well established technique in conservation the results are still variable and unpredictable[1] and highly dependent on the characteristics of the poultice in relation to the material to be desalinated. In case tiles are removed from the support they can then be desalinated by immersion in distilled water[2].

In the present work the possibility for using electrokinetic extraction for removal of salts from tile panels inclusive the wall behind is discussed. Electrokinetic extraction of salts from building stone is a method under development. Removal percentages for NaCl from single bricks or sandstones of 99% have been obtained in laboratory scale and encouraging results have been obtained in a pilot scale experiment with a salt contaminated masonry of an old house. Preliminary laboratory experiments with electrokinetic desalination of a single tile were conducted and reported here. The aim being to test if the method can be used for removing damaging salts from tiles as well. Thus the first step is taken to investigate if the electrokinetic desalination method can be developed to a method which can be used for conservation of the important heritage these tile panels are.

PRINCIPLE OF ELECTROKINETIC DESALINATION

Electrokinetic extraction of ions from stone

The major transport mechanism for salt ions in a porous, moist stone in an applied electric field is electromigration. Positive ions will move towards the negative electrode (the cathode) and negative ions will move towards the positive electrode (the anode). As time passes the ions will be depleted from the stone and concentrate in the vicinity of the electrodes. In salt contaminated stones, ions of the salts will be transported towards the electrodes as shown in figure 1. As the ions are removed, equilibrium will change towards dissolution of more nucleated salts (if present) and the new ions are extracted from the stone as well, and eventually both dissolved and nucleated salts are removed.

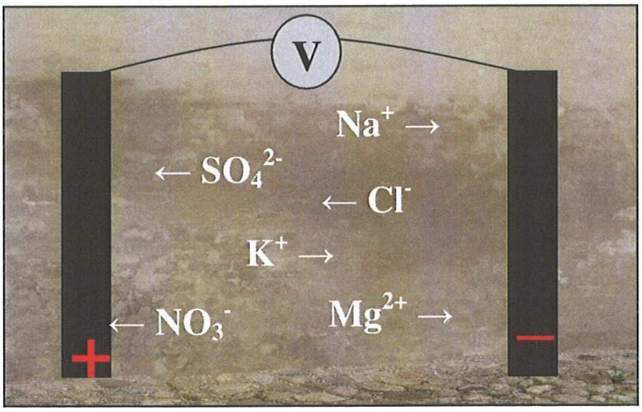

Figure 1 - Principle of electrokinetic desalination. Ions are moving in the moist pores towards the electrodes as a result of the applied electric DC field.

It is necessary to place the metallic electrodes (from where the electric current is supplied to the stone) in a poultice, which serves as medium for (a) concentrating the arriving ions, (b) ensuring good electrical contact between stone and metallic electrode and (c) neutralizing the acid produced at the surface of the metallic anode.

In metallic electrodes the electric current is carried by electrons, whereas in the pore water the current is carried by ions. The processes that transform the current carried by electrons to current carried by ions and vice versa are described as electrode processes. Which electrode processes occur depend on the electrode material, the type and concentration of ions in the pore water and the applied potential. There are always oxidation processes at the anode and reduction processes at the cathode. In the electrokinetic desalination experiments of the present work inert electrodes were used. The dominating electrode processes are then electrolysis of water:

At the anode: $H_2O \rightarrow 2H^+ + ½ O_2 (g) + 2e^-$
At the cathode: $2 H_2O + 2e^- \rightarrow 2OH^- + H_2 (g)$

If the removed chloride ions reach the surface of the anode Cl_2 gas can additionally be formed from the anode process: $2Cl^- \rightarrow Cl_2 (g) + 2e^-$

Electrolysis influences the pH around the electrodes. Around the cathode the environment becomes alkaline and around the anode it is acidified. The pH changes must be taken into account when designing the electrode compartments, since especially acidification can damage the stone. A poultice which was a mixture of kaolinite and $CaCO_3$ was used in at the electrodes, and in this poultice the $CaCO_3$ neutralized the acid. This type of poultice was previously subject for a patent application in relation to electrokinetic desalination[3]. The development for the patent application also included a clay mixture for neutralizing the base produced at the cathode, but this mixture was not used in the present work. Here the same clay poultice was used in both anode and cathode compartments.

PREVIOUS EXPERIENCES FROM SANDSTONE, BRICKS AND BRICK MASONRY

Electrokinetic desalination experiments have previously been conducted in laboratory scale with single stone/bricks and very good results have been obtained. Some examples of experimental results with chloride removal are shown in table 1. These results have been obtained with single sandstones/bricks which were water saturated initially. The results shown have been chosen from previously published successful results. To evaluate the initial and final Cl concentrations in the stones in table 1 comparison with the concentrations given in the Austrian ÖNORM B 3355-1 "Trockenlegung von Feuchtem Mauerwerk – Bauwerksdiagnostik und Planungsgrundlagen" (Dehumidification of masonry - Building diagnostics and planning principles) is relevant. The chloride concentrations are divided into three categories in this norm: (a) < 0.03 wt% – no risk, (b) 0.03 – 0.10 wt% – individual evaluation necessary, and (c) > 0.10 wt% – active salt removal advised. The experimental results given in table 1 thus show that it is possible to remove chloride from a concentration in the highest category where active salt removal is advised to a harmless concentration. Most work has so far been conducted with chlorides, but nitrates have also been removed successfully from yellow bricks[4].

The duration of the electrokinetic Cl removal in laboratory scale was up to 3 weeks (table 1) and no limitations originating from the stone type was seen. A water content of 7% is sufficient for the desalination to occur and most likely this is not the lower limit for water content. The removal percentages in all four cases shown in table 1 were approximately 99%.

Table 1: Results previously obtained in laboratory scale with electrokinetic desalination of slingle stones.

	Water content (%)	**Duration (d)**	**Charge transfer/mass (C/kg)**	**Initial Cl^- concentration (wt%)**	**Final Cl^- concentration (wt%)**
Cotta sandstone[5]	8	21	37000	0.41	0.005
Posta sandstone[5]	7	18	44000	0.34	0.005
New yellow brick[6]	17	9	7400	0.10	0.0009
Red brick (handcrafted)[7]	13	21	29000	1.0	0.005

Desalination of brick masonry has also been tested in a pilot experiment[8] (see figure 2). Here new electrode units were designed. The electrodes are placed on the masonry surface with screws and after the action the only physical sign on the wall is the holes from the screws. Each electrode unit was a box with a movable bottom, which can be pushed towards the masonry by tightening screws connected to springs at the back of the box. Inside the electrode unit, placed directly on the movable bottom, was a metallic mesh, which served as electrode and between the electrode and the masonry was the clay poultice in a layer of approximately 3 cm in thickness.

In the pilot scale experiment all electrodes were placed on the outer surface of a masonry from an old farm house, which had served different purposes. When placing the electrodes on the same side of the masonry, the electric field is strongest in the outer part of the masonry where the salts are. The masonry had huge problems with paint/plaster peeling in the height of 30-55 cm due to salt contamination. Figure 2 shows the pilot experiment which consisted of 6 electrodes placed as 3 sets, each set having the internal distance of 35 cm and own power supply. In a full scale action the electrodes would not have been placed as such sets in this way. The electrodes would rather have been placed with the same mutual distance and be connected to the same power supply to cover a larger area, however, in the pilot experiment it was beneficial to be able to follow each set of electrodes separately for interpretation of the results. The electrodes in the pilot experiment were 50 cm long and they were held with screws (and plastic plugs) to the masonry.

The drilling powder from the holes made for fastening the electrode units were collected (powder from each hole separately) and the concentrations of chloride, nitrate and sulphate were measured in the powder. The analysis showed that the concentrations were significantly higher 70 cm above ground compared to 30 cm.

During the desalination a DC current of 40 mA was applied to each electrode set. After two periods of 2 months with electrokinetic extraction new drilling powder from several places were taken in the height of 70 cm above ground. Table 2 shows the average concentrations in the drilling powder before and after electrokinetic extraction in the pilot scale experiment.

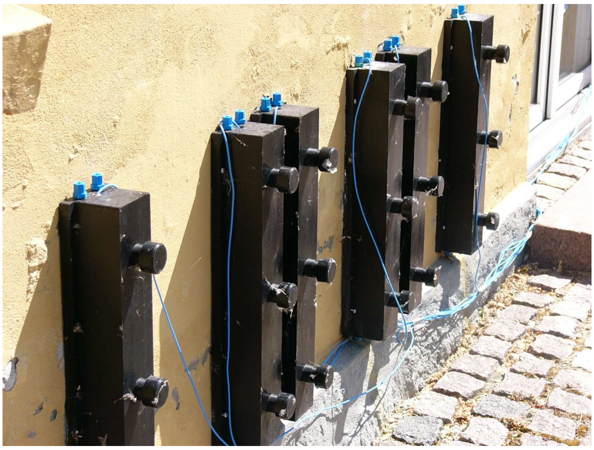

Figure 2 - Pilot scale experiment on salt contaminated masonry. The electrodes were placed in 3 sets, all at the outer surface of the masonry.

Table 2 - Average concentrations in masonry before and after electrokinetic desalination in pilot scal[8].

	Initially	**After extraction**
Cl^- (wt%)	0.06 ± 0.05	0.03 ± 0.03
NO_3^- (wt%)	± 0.07	0.01 ± 0.02
SO_4^{2-} (wt%)	0.68 ± 0.46	0.46 ± 0.42

Sulphates had the highest initial average concentration in the masonry in the actual height of 70 cm (table 2) and the average concentration far exceeded the highest concentration from ÖNORM B 3355-1 and actually all initial samples exceeded this value. The mean initial concentration of chloride and nitrate did not exceed the upper value of the ÖNORM B 3355-1, however it is seen from the standard deviations in table 2 that the concentration in the samples varies significantly. Few samples showed problematic concentrations both in relation to nitrate and chloride.

During the electrokinetic extraction the average concentration of all three anions had decreased (table 2). After the electrokinetic extraction the concentration of chloride and nitrate was below the upper limit of the ÖNORM B 3355-1 in all samples. For sulphate the concentration in 5 out of 9 samples still exceeded this upper limit, so the concentration of sulphate was not sufficiently decreased in all wall section during the pilot experiment. Unfortunately the pilot experiment could not proceed for a third period due to time restrictions of the actual project. It is thus not known, if longer treatment time could have decreased the sulphate concentration sufficiently. Indications were however seen on a lower mobility of sulphate (about half) during the second period compared to the first period, emphasising that the dissolution rate of sulphates may be the rate limiting step[8]. The dissolution rate of different salt types must be studied in order to be able to predict the duration of an action. The salts, which are problematic in relation to salt decay of porous building stone, are problematic due to dissolution-nucleation cycles, and these salts are thus dissolved at some stages under normal environmental conditions in the actual place.

A preliminary pilot scale experiment has also been conducted on a wall section with painted murals on one side[9]. The wall section was made as a test wall in1994 with materials of the same type as found in Danish medieval churches. The wall section was contaminated with NaCl by spraying over a long period of time and peeling of the mural had started. The wall section was placed in a laboratory and water was sprayed to the surfaces for moistening the dry wall. Electrodes were placed on the side of the wall section without murals and an electric field was applied for 2 weeks. The major conclusions from this experiment were that no pH changes in the wall were seen (highly important in relation to avoid dissolution of the pigments and lime mortar) and that the desalination was fastest in the areas where moistening was easiest.

In summary, the actual stage of development for electrokinetic desalination is that the method has shown highly efficient for treatment of single stones in laboratory, and encouraging results have been obtained through a pilot scale experiment on salt infected brick masonry. The major questions to be addressed in the future in relation to masonry are dissolution rate of the most common problematic salts and influence from an unevenly distributed moisture content on the electric field. When turning to sandstone sculptures there is also the question on the distribution of the electric field and optimal placement of electrodes at very uneven surfaces in order to ensure that salts are extracted efficiently from all parts of the sculpture.

Discussion on the possibility of using electrokinetics for desalination of tile panels

In relation to salt induced decay of tile panels, the salts are typically found in the tiles themselves, in the mortar in which they are attached to the wall and in the wall behind. Efficient desalination includes removal of the salts from all three layers in order to avoid the problem to returning shortly after the action.

One important advantage of electrokinetic desalination compared to traditional poulticing (next to the more controlled transport mechanism for salt out from the material) is that the poultice with electrodes do not have to cover the whole surface to be desalinated. Further the electric field can act in significant depth of the material. The electric field in the material between the electrodes will be strongest where the conductivity is highest and that is where the ionic concentration is highest (everything else equal). Thus the electric field will act strongest exactly where the salts are concentrated even though the electrodes are not placed directly in this place. This means that for desalination of tile panels inclusive mortar and wall behind can be done by removing few tiles and place electrodes of the same size as the removed tile in the hole. This ensures limited intrusion in what regards the whole panel and the desalination can be performed in situ and include the material behind the tiles. The removed tiles can be placed in the original position in the panel after the desalination and there will be no visual sign of the intervention.

The possibility for electrokinetic desalination of the tiles themselves has not previously been tested. Results from preliminary experiments with desalination of a single tile are described in the following.

EXPERIMENTAL

Tile for the experiments and contamination with NaCl

One Portuguese XIX century tile was used for these preliminary experiments. The tile had never been in use. The tile was cut into 4 segments as shown in figure 3. The thinnest segment (to the right) was used as blind sample for measurement of the original chloride content of the tile. The three other segments were submerged in 15 g/L NaCl solution for 7 days. The water content (water/dry mass) was 16% after the submersion. One of the segments was used as reference whereas electrokinetic desalination was tested on the remaining two segments. The segments were weighed before and after the submersion for calculation of water content.

Figure 3 - The tile used for the experiments (after segmentation). The thin slice at the right was a blind sample. The remaining slices were submerged in a NaCl solution. One segment was subsequent used as reference and two segments were used for electrokinetic desalination.

Experimental procedure for desalination of single tile

The reference segment and the two segments for electrokinetic desalination were carefully wrapped in several layers of plastic film after the submersion in order to avoid evaporation during the experiments. The segments were placed with the glazing down. Two rectangular holes (approximately 3 cm x 3 cm) were cut in the plastic film in the upper side of each end of the two segments for the desalination experiments. A rectangular plastic frame of 3 cm height was placed over the hole. Poultice of kaolin clay and $CaCO_3$ (as described in [3]) was filled into the frame. On top of the poultice an electrode mesh was placed. The electrode was covered with plastic film. Figure 4 shows the experimental setup.

Current was passed through the tile segment for 6 days. During the first 2 days, the current was 5 mA and the voltage about 10V. At the third day, the resistivity of the system had increased dramatically and the maximum voltage of the power supply (136 V) was reached and the current subsequently decreased to less than 1 mA. The current decreased all through the last 4 days of the experiment and ended at 0.4 mA.

Figure 4 - Setup for electrokinetic desalination of tile segment. The electrode meshes were connected to the power supply

At the end of the experiments the segment was separated into 5 pieces with hammer and chisel perpendicular to the length. Each piece was weighed, dried at 105ºC for 24 hours and weighed again for calculation of water content. The dried pieces were powdered by hand in a mortar. Extractions in distilled water (10 g powdered tile in 25 ml) were made with this powder and after 24 hours agitation pH was measured with a pH electrode directly in the suspension, which was subsequently filtered and the Cl concentration was measured by titration and the Na concentration with AAS.

Results and discussion

Profiles of Cl and Na concentrations in the reference tile segment and in the tile segments where electrokinetic desalination was tested (EK) are shown in figure 5a and 5b, respectively. The tile segments were desalinated successfully. At figure 5a the limiting concentrations from ÖNORM B 3355-1 are shown together with the profiles from the experiments. It is seen that initially the chloride concentration exceeded the upper limit from the ÖNORM where desalination is advised and after the treatment the concentration was decreased to a level less than the lowest limiting concentration from the ÖNORM where the concentration is considered harmless. The chloride concentration in the anode poultice was about 0.28 wt% and in the cathode poultice 0.009 wt% clearly showing the effect of electromigration which will transport the negatively charged chloride towards the anode. The sodium was removed as efficiently as the chloride.

The next experiments will be conducted with a shorter duration to see if the desalination was actually concluded after the 2 days of applied current where the resistivity increased dramatically. The increase may very well be an indication of this.

The pH in the reference tile was 9.6 ± 0.4% and the pH of the EK tiles were 9.9 ± 0.4%. The pH was not decreased closest to the anode and the poultice neutralized the produced acid from the anode process successfully

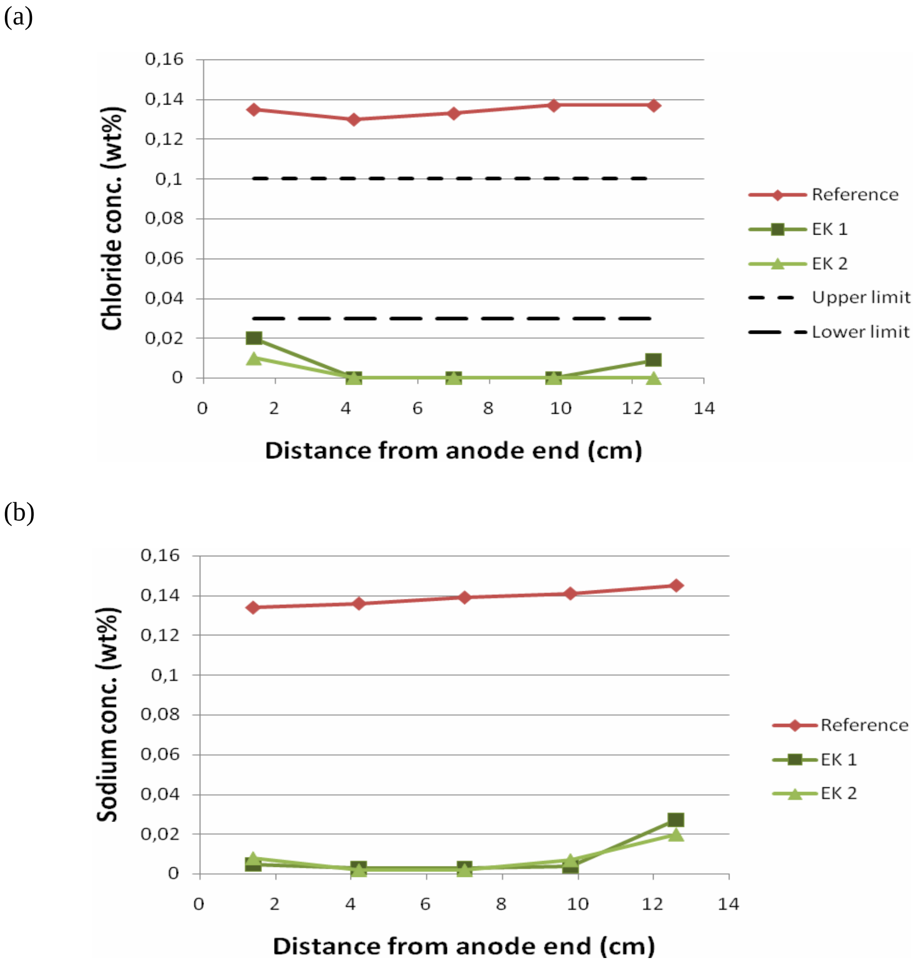

Figure 5 - concentration profiles in the tile segment after the electrokinetic experiments (EK) in comparison with the reference experiment where no current was applied and the upper and lower limits of the ÖNORM B 3355-1.

CONCLUSIONS

Electrokinetic desalination of sandstone monuments and stone sculptures is a conservation method under development. The results so far has been highly encouraging both in laboratory and pilot scale. In the present paper preliminary experiments with electrokinetic desalination of glazed tiles were conducted and removal efficiencies of 96% for chloride in less than 6 days were obtained. On basis of this it is suggested to continue the research to cover electrokinetic treatment of tile panels. The method may be applicable for salt removal from both tiles and the wall behind.

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REFERENCES

1. SAWDY, A; HERITAGE, A; and PEL, L. (2008). A review of salt transport in porous media, assessment methods and salt reduction treatments. Proceedings from the International Conference on Salt Weathering on Building and stone Sculptures, 22-24 October, Copenhagen, Denmark.
2. GOMES, M. M. M. & MONTEIRO, J. P. (1996). Conservation and Restoration of Azulejos – Portuguese Tiles. Published by Ricardo do Espírito Santo Foundation. Lisbon, 1996 (ISBN 972-8253-09-5).
3. RÖRIG-DALGAARD, I., OTTOSEN, L.M. (2008) Patent application 08154186.4-Method and device for removing an ionic impurity from building structures
4. OTTOSEN, L.M., RÖRIG-DALGAARD, I. (2007) Electrokinetic removal of $Ca(NO_3)_2$ from bricks to avoid salt induced decay. *Electrochimica Acta*, *52(10)*, 3454 – 3463
5. OTTOSEN, L.M. (2009) Electrokinetic removal of halite from Cotta and Posta sandstones. Submitted
6. OTTOSEN, L.M., RÖRIG-DALGAARD, I. (2009) Desalination of a brick by application of an electric DC field. *Materials and Structures*, In press
7. RÖRIG-DALGAARD, I. 2008 Preservation of masonry with electrokinetics – with focus on desalination of murals. PhD Thesis. Department of Civil Engineering, Technical University of Denmark.
8. OTTOSEN, L.M., RÖRIG-DALGAARD, I., VILLUMSEN, A. (2008) Electrochemical removal of salts from masonry - Experiences from pilot scale. Salt Weathering on Buildings and Stone Sculptures. Copenhagen, 22-24 October 2008, 341-350
9. RÖRIG-DALGAARD, I., OTTOSEN, L.M. and CHRISTENSEN I.V. (2008). Desalination of a wall section with murals by electromigration. Proceedings from the International Conference on Salt Weathering on Building and stone Sculptures 22-24 October, pp. 361-371, Copenhagen, Denmark.