

# Electrokinetic desalination of glazed ceramic tiles

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**Abstract** Electrokinetic desalination is a method where an applied electric DC field is the driving force for removal of salts from porous building materials. In the present paper, the method is tested in laboratory scale for desalination of single ceramic tiles. In a model system, where a tile was contaminated with NaCl during submersion and subsequently desalinated by the method, the desalination was completed in that the high and problematic initial  $\text{Cl}^-$  concentration was reduced to an unproblematic concentration. Further conductivity measurements showed a very low conductivity in the tile after treatment, indicating that supply of ions from the poultice at the electrodes into the tile was limited. Electroosmotic transport of water was seen when low ionic content was reached. Experiments were also conducted with XVIII-century tiles, which had been removed from Palacio Centeno (Lisbon) during renovation due to damage of the glazing from the presence of salts. These tiles were severely contaminated with both chlorides and nitrates, and one of the tiles also contained sulphates though at a low concentration. The charge transfer was too low in the experiments to obtain full desalination, but promising results were obtained as significant decreases ( $>81\% \text{Cl}^-$ ,  $\sim 59\% \text{NO}_3^-$  and  $\sim 22\% \text{SO}_4^{2-}$ ) were seen.

**Keywords** Desalination · Salt decay · Azulejo tile · Electrokinetics · Electroosmosis

## 1 Introduction

Ceramic tiles are an important part of the cultural heritage in many countries as The Netherland and Portugal. The Portuguese tiles are named Azulejo and are used for decoration of inner and outer walls of churches, gardens, private houses, railway stations and a series of other buildings. The Azulejos are worldwide appreciated, but unfortunately many tile panels suffer from severe decay. 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 crystallization when water evaporates. Cycles of dissolved and nucleated salts caused by changes in relative humidity are escalating the damage. 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, which 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].

Electrokinetic extraction of salts from building stone to avoid salt induced decay is a method under development. In the present work the possibility for using electrokinetic extraction for removal of salts from tiles is investigated. Electromigration which is the major transport mechanism

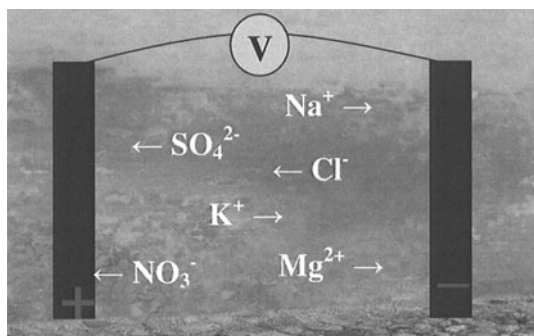
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for removing salts from building stone is also utilized for repair and maintenance purposes in concrete structures here for chloride removal to prevent reinforcement corrosion. The development of electrokinetic methods for chloride removal from concrete was initiated in the early 1970s in the United States by the Federal highway Administration [3]. An overview of the methods for concrete repair can be found in [3, 4] and some case studies described in [5]. Good results have previously been obtained with this method for desalination of bricks and sandstones and removal percentages for NaCl from single bricks of 99% have been obtained in laboratory scale [6] and further encouraging results have been obtained in a pilot scale experiment with a salt contaminated masonry of an old house [7]. Experiments with electrokinetic desalination of single tiles were conducted and are reported in the present paper. The aim being to test if the method can be used for removing damaging salts from tiles, as well. Thus the first step is here 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.

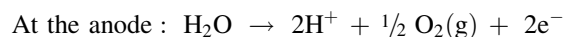
Electromigration is the major transport mechanism for salt ions in a porous, moist building material as a tile in an applied electric field. Positive ions will move towards the negative electrode and negative ions will move towards the positive electrode. As time passes the ions will be depleted from 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 Fig. 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.

It is necessary to place the metallic electrodes (from where the electric current is applied to the tile) in a poultice, which serves as medium for (a) concentrating the arriving ions, (b) ensuring good electrical contact between



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

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:



If the removed chloride ions reach the surface of the anode  $\text{Cl}_2$  gas can additionally be formed from the anode process:  $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ .

Electrolysis influences the pH around both 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  $\text{CaCO}_3$  was used at the electrodes, and in this poultice the  $\text{CaCO}_3$  neutralized the acid. This type of poultice was previously subject for a patent application in relation to electrokinetic desalination [8]. The same clay poultice was used in both anode and cathode compartments in the present experiments.

In relation to salt 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 returning shortly after the action.

One important advantage of electrokinetic desalination compared to traditional poulticing (next to offering 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 be strongest exactly where the salts are concentrated even though the electrodes are not placed directly in this place. One idea for electrokinetic desalination of a tile panel inclusive mortar and wall behind is removing few tiles and place electrodes

here. 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 first step towards developing such method for electrokinetic desalination of tile panels is reported in the present paper, as the possibility for electrokinetic desalination of the tiles themselves is tested. Experiments are conducted with two different Portuguese tile types. XIX-century tiles, which were spiked in NaCl in laboratory, and XVIII-century tiles removed from the structure in Lisbon due to salt damage of the glazing.

## 2 Experimental

### 2.1 Tiles for the experiments

Two types of tiles were used in the experiments. The first are XIX-century Portuguese tiles that have never been in use. The second type of tile is from the XVIII century and was removed from Palacio Centeno (in Lisbon) during renovation works due to severe salt damage. The area of the tiles was about 14.3 cm × 14.3 cm, and the XIX-century tiles were about 0.9 cm thick and the XVIII-century tiles 1.2 cm thick.

#### 2.1.1 XIX-century tiles

The tiles were each cut into 4 segments as shown in Fig. 2a. The thinnest segment (to the right) was used as blind sample for measurement of the original chloride content of the tile. The other thicker segments were submerged in 15 g/L NaCl solution for 7 days. One of the segments was used as reference (experiment XIX-a) whereas electrokinetic desalination was tested on 4 of these segments (experiments XIX-b to e). The segments were weighed before and after the submersion for calculation of water content.

**Fig. 2 a** One of the XIX-century tiles used for the experiments (after segmentation). The thin slice at the right was a blind sample and the remaining slices were used for electrokinetic desalination experiments, **b** the salt damaged XVIII-a tile



#### 2.1.2 XVIII-century tiles

One of the XVIII tiles is shown in Fig. 2b and it is seen that the glazing is lost at the outer edge of the tile, which is a common pattern when tiles are salt contaminated. The electrokinetic desalination experiments with the two XVIII tiles were conducted without segmentation prior to the desalination. The tiles, which had dried at room temperature in the laboratory was wetted by spraying distilled water on the back side (opposite side of the glazing). Little water was sprayed on the tile and it was left in a plastic bag for some days. This procedure was repeated 7 times until the weight had increased with 2.8% where it was observed that the water was penetrating the tile only slowly after the spraying.

The experiments with spiked tiles were made as model experiments with a single salt and a known initial concentration. Prior to the desalination the salt composition and concentrations were unknown in the salt damaged XVIII-century tiles, as the analytical methods are destructive and a relatively high variation in salt concentrations are expected between tiles, even from the same panels. Further significant variation in each tile is expected as evaporation of water and subsequent concentration of salt from the front of the tile occurs less through the central parts of the tile where glazing is intact in comparison to the outer parts where the glazing is lost.

### 2.2 Electrokinetic desalination experiments

The tile segments or tile for the desalination experiments were wrapped in several layers of plastic film to minimize evaporation. The tile and segments were placed with the glazing down. The XIX tile reference segment was left wrapped in plastic. In the plastic film of the other XIX-segments two rectangular holes (approximately 3 cm × 3 cm) were cut in the upper side of each end for the electrodes. A rectangular plastic frame of 3 cm height was placed over the hole. Poultrice of kaolin clay and CaCO<sub>3</sub> (as described in [5]) was filled into the frame. On

top of the poultice an inert electrode mesh was placed. The electrode mesh was finally covered with a thin layer of poultice and a plastic film and connected to the power supply. Figure 3 shows this experimental setup.

As the level of salt contamination is expected to vary significantly in the XVIII tiles there is no reference experiment to these two experiments. The setup used for these tiles was as described for the XIX tiles, the only difference being the length of the plastic frame with poultice, which here covered the full length of the tile (14.3 cm).

This investigation includes seven experiments. The dry weight, initial water content, current range, voltage range and duration of the experiments are shown in Table 1.

The power supply was set to supply a constant DC current during all experiments, however, the voltage increased during the experiments with XIX tiles and reached the maximum for the power supply and subsequently the current decreased. In experiment XVIII-a the current of 5.0 mA was maintained all during the experiment. In experiment XVIII-b the current was changed manually several times in order to avoid the maximum of the power supply to be reached, but also at the same time to apply a relatively high current to have as short duration as



**Fig. 3** Setup for electrokinetic desalination of tile segment. The electrode meshes were connected to the power supply

possible. During the experiments voltage and current were measured approximately every 24 h.

Water was added the poultice or the tile in some of the experiments. In experiment XIX-b few mL of distilled water was added on top of the clay poultice on the 2nd and 5th day to see if this could lower the overall resistivity of the experiment. No water was added to the other XIX tile experiments and experiment XVIII-a. During the 24 days of experiment the XIX-b tile was unwrapped 4 times where distilled water was sprayed on the back side of the tile with an atomizer (days 7, 8, 12 and 22). Further the poultice was changed after 7 days and after 22 days distilled water was added the poultice.

At the end of the experiments tiles and tile segments were segmented into pieces with hammer and chisel. Five pieces of approximately the same size were made perpendicular to the length of the XIX-century tile segments and the pieces were numbered from 1 to 5, where 1 was closest to the anode. The XVIII tiles were separated into 8 pieces. The tile was first broken into two pieces running from anode towards cathode (A and B). The two pieces were subsequently separated into 4 segments each. Segment 1A and 1B had been covered by the anode poultice, segments 2 and 3 had been between the electrodes, and finally segment 4A and 4B had been covered by cathode poultice during the desalination experiment.

### 2.3 Analytical

Each tile piece was weighed, dried at 105 °C for 24 h 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 suspended in 25 mL) were made and after 24 h agitation pH was measured with a pH electrode and conductivity with a conductivity electrode directly in the suspension, which was subsequently filtered and the concentrations of Cl<sup>-</sup> (XIX tiles) and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (XVIII tiles) were measured by ion

**Table 1** The conducted experiments

	Dry weight (g)	Initial water content (%)	Current (mA)	Voltage (V)	Duration (days)
XIX-a	85.8	15.8	0	0	6
XIX-b	88.6	16.4	5.0 → 0.3	11–137	6
XIX-c	99.1	16.4	5.0 → 0.3	11–137	6
XIX-d	89.8	15.2	2.0 → 1.0	6–136	4
XIX-e	92.3	15.5	2.0	5–16	2
XVIII-a	473.3	–	5.0	3–4	7
XVIII-b	458.8	–	5.0–15.0	7–123	24

XIX-a is reference experiment to the electrokinetic desalination experiments XIX-b to e. The two XVIII experiments are conducted with original and salt contaminated tiles (the initial water content of the two original tiles is not known as they were not oven dried before the experiments)

chromatography. The same analytical procedure was followed for the corresponding analyses of the poultice.

### 3 Results and discussion

#### 3.1 Voltage and current during experiments

In experiments XIX-b and XIX-c the current was set to 5 mA, but already at the beginning of the 2nd day the maximum voltage for the power supply (137 V) was reached and thus the current started to decrease as the

overall resistance kept increasing. The current was adjusted to 1 mA, but the voltage kept increasing during day 2 and it was lowered again to 0.3 mA, which was the current for the remaining time of the two experiments (see Fig. 4a). The overall voltage of experiment XIX-b was lower than in experiment XIX-c most likely due to the addition of distilled water at the top of the clay poultice in XIX-b. This shows that the water content may have been too low here after some days, but even after addition of water, the resistivity was too high to maintain the current at 5 mA.

As the current of 5 mA in the first two desalination experiments could not be maintained for more than

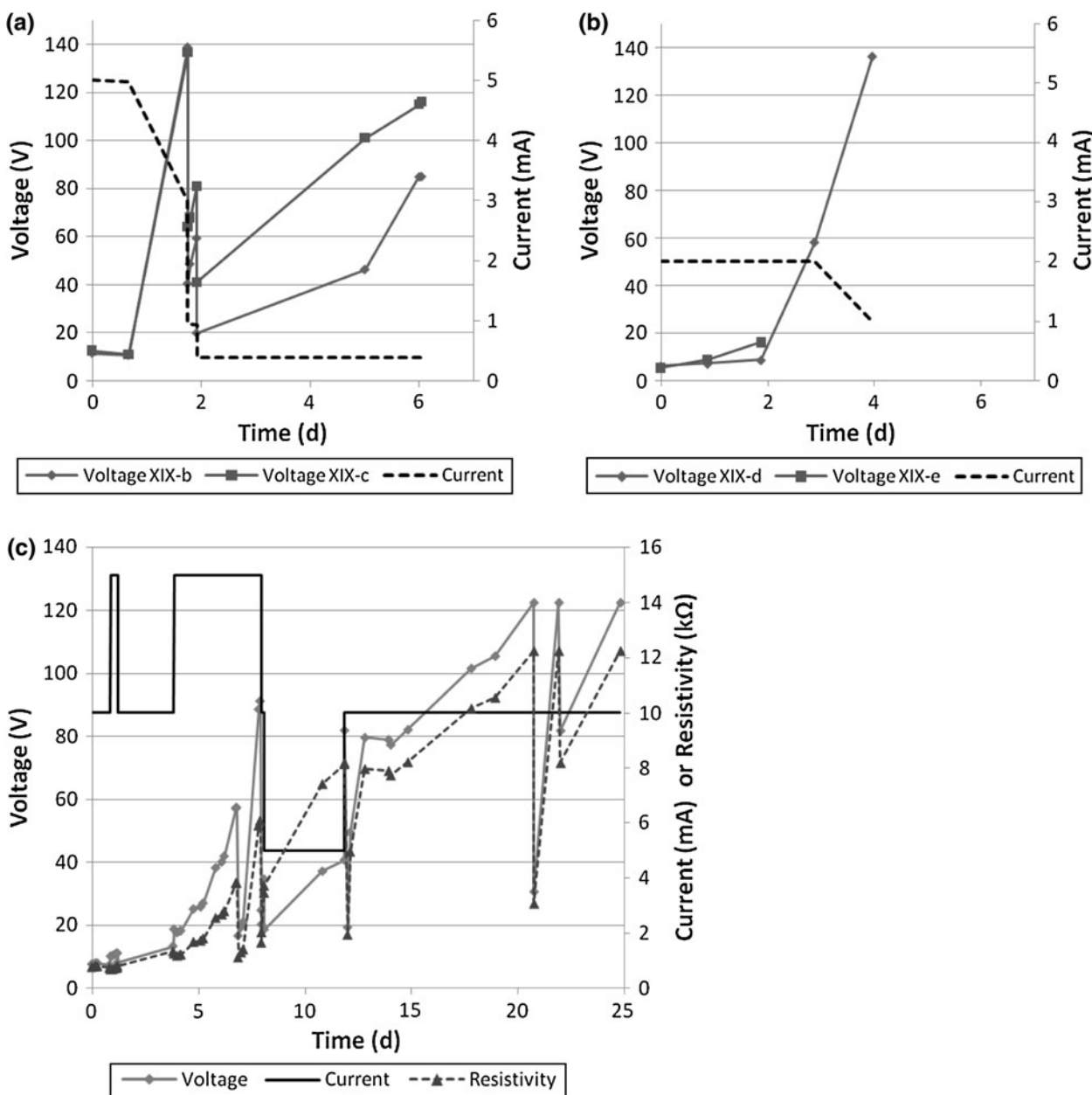


Fig. 4 Voltage, current and resistivity during a experiments XIX-b and c, b experiments XIX-d and e, and c experiment XVIII-b



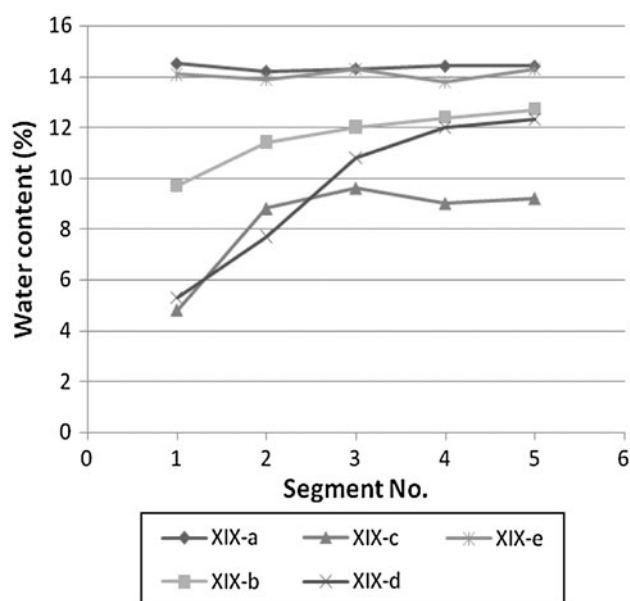
1–2 days, the current in the next two experiments XIX-d and XIX-e was set to 2 mA (Fig. 4b). This current was maintained for the 2 days of experiment XIX-e and in experiment XIX-d the current was maintained until day 5, where the current started to decrease as the maximum of the power supply was reached. When the voltage in experiment XIX-d reached maximum for the power supply, the experiment was stopped to see if the increase was caused by the desalination being concluded. The duration of experiment XIX-e was chosen to be 2 days since this represents the maximum duration where the voltage was at the lower level in experiment XIX-d.

In experiment XVIII-a the current was constant at 5.0 mA all through the 7 days of the experiment and the voltage varied only slightly between 2.6 and 3.6 V. The low and almost stable voltage shows that there was a high conductivity in all parts of the setup.

In experiment XVIII-b the current was stepwise constant as seen in Fig. 4c. During the 1st day the current was 10 mA (chosen higher than experiment XVIII-a as the voltage in this experiment was very low) and the voltage decreased slightly from 7.6 to 7.3 V. It was decided to see if the current could be 15 mA without increasing voltage, but during 6 h the voltage increased from 10.1 to 11.1 V and the current was adjusted to 10 mA again for the next 3 days. Then as the voltage was still relatively low (13 V) the current was increased once more to 15 mA for 4 days where the voltage increased to 91 V. From Fig. 4c it can be seen that the voltage decreased sharply for a short period after 7 days. At this point distilled water was sprayed to the tile, which caused an immediate decrease in voltage from 57.4 to 16.6 V. Two hours before spraying water to the tile the clay poultice was changed but this caused no decrease in voltage. This shows that the major resistance in the system was due to too low water content in the tile. The current was then kept 5 mA for almost 4 days and increased again to 10 mA which was the current for the rest of the experiment. The resistivity increased generally all through these periods, however sharp and short decreases were seen when water was sprayed on the tile. This shows that a low water content in some parts was causing a high resistivity, but the effect of the added water was short. In the measurements of the overall water content in the tile pieces at the end of the experiments, there is no indication of where the problem could be, as the water content was more than 9.8% in all pieces. This may be a sign of a local phenomenon.

### 3.2 Water content

The profiles of water content in the XIX-century tiles at the end of experiments are shown in Fig. 5. It is seen that there is a tendency for the water content to be lowest in the



**Fig. 5** Water profiles in reference experiment XIX-a and after electrokinetic experiments XIX-b to e (1 closest to the anode and 5 closest to the cathode)

anode end in experiments XIX-b to d, which is probably caused by electroosmosis (movement of water in a porous material in an applied electric DC field). For one type of red bricks submerged in NaCl as single salt it has been found that during electrokinetic desalination electroosmosis starts when the  $\text{Cl}^-$  concentration reaches about 100 mg/kg [9]. At higher concentrations the conductivity in the bulk pore water is higher than in the electric double layers at the internal surfaces and subsequently the major part of the current passes in the bulk. At low ionic concentrations the conductivity is oppositely highest within the electric double layers, which causes the current mainly to flow here and electroosmosis starts [9].

The final water content in the XVIII tiles was about  $11.0 \pm 0.4\%$  and  $10.5 \pm 1.0\%$ , which is slightly lower than initially for the XIX tiles but at the same level as XIX-b. The XIX tile segments were water saturated during submersion whereas water was sprayed on the back of the XVIII tiles. It is interesting to find the lower limit where the water content is just sufficient for the desalination to occur in relation to salt contaminated and fragile museum tiles, since these should be added a minimum of water in order to limit the damage by the treatment.

### 3.3 Overall desalination results

The average concentrations of pH, conductivity, Cl (XIX tiles) and  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (XVIII tiles) are shown in Table 2. The final water content measured for the whole tile segment/tile is also given.

**Table 2** Average pH, conductivity, water content,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in the tiles at the end of the desalination experiments

	pH	Conductivity (mS/cm)	$\text{Cl}^-$ (mg/kg)	$\text{NO}_3^-$ (mg/kg)	$\text{SO}_4^{2-}$ (mg/kg)	Final water content (%)
XIX-a	9.6 ± 0.4	1.9 ± 0.2	1340 ± 30	–	–	14.3
XIX-b	10.0 ± 0.4	0.3 ± 0.2	62 ± 96	–	–	11.5
XIX-c	9.9 ± 0.5	0.3 ± 0.1	20 ± 46	–	–	8.2
XIX-d	10.4 ± 0.5	0.4 ± 0.3	16 ± 36	–	–	9.5
XIX-e	10.4 ± 0.6	1.1 ± 0.2	440 ± 380	–	–	14.2
XVIII-a	8.5 ± 0.2	12.6 ± 3.2	3270 ± 1050	5530 ± 1560	14 ± 28	11.0 ± 0.4
XVIII-b	9.2 ± 1.0	5.1 ± 2.0	680 ± 440	3490 ± 1610	105 ± 40	10.5 ± 1.0

To evaluate the initial and final anion concentrations ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) in the tiles comparison to the concentrations given in the Austrian Önorm B 3355-1 “Trochkenlegung von Feuchtem Mauerwerk—Bauwerksdiagnostik und Planungsgrundlagen” (Dehumidification of masonry—Building diagnostics and planning principles) is used. This norm gives two threshold values for each of these anions. If the concentration is below the lowest of these values there is no risk, and if the concentration exceeds the highest value active salt removal is advised. In between the two values, individual evaluation at the specific site must be performed. The threshold values are (lowest/highest) 300/1,000 mg  $\text{Cl}^-$ /kg, 500/1,500 mg  $\text{NO}_3^-$ /kg and 1,000/2,500 mg  $\text{SO}_4^{2-}$ /kg.

From Table 2 it is seen that the average  $\text{Cl}^-$  concentration in the XIX-a reference tile exceeded the upper threshold value and thus the concentration is problematic. After electrokinetic desalination the concentration decreased significantly, and in the three experiments XIX-b to d, the average concentration was well below the lower value.

The conductivity at the end of the XVIII-a and b desalination experiments was even much higher than in the XIX reference tile initially and as seen in Table 2, the high conductivity is caused by a severe contamination with  $\text{NO}_3^-$  and  $\text{Cl}^-$  since the concentration of both exceeds the threshold values. The concentration of  $\text{SO}_4^{2-}$  on the other hand was well below the lower threshold value from the Önorm B 3355-1.

### 3.4 pH changes in the tiles

Due to water electrolysis at the electrodes, acid is produced at the surface of the anode and base at the cathode as described in the introduction. The carbonate rich poultice was used in order to neutralize the acid and subsequent to avoid acidification of the tile. The clay poultice did neutralize the acid efficiently as pH in the anode poultice was unchanged 8.8 at the end of all the experiments. The base produced at the cathode was not in the same way directly

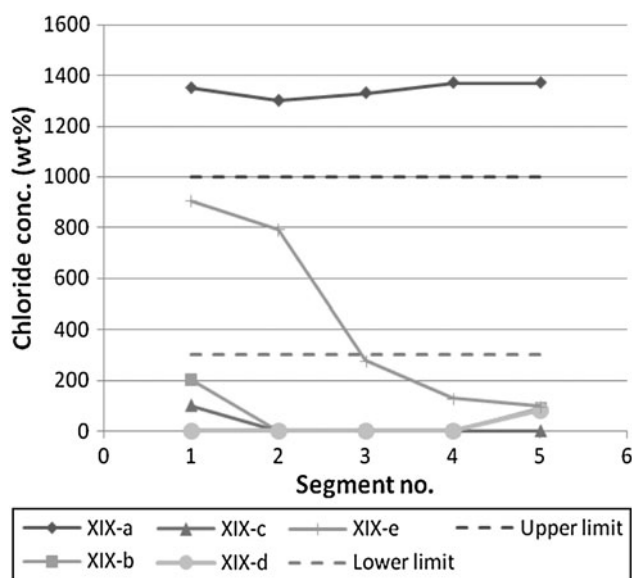
chemically neutralized by the used poultice and pH in the cathode poultice increased from 8.8 to between 11.1 and 11.4. The pH in the tile segments below the cathode was between 10.7 and 10.8 at the end of the experiments XIX-b to e. This is an unwanted pH increase and to avoid it a new cathode poultice must be developed, which neutralizes the produced base. The pH increase is problematic as the measured ionic mobility of hydroxyl ions  $\text{OH}^-$  is exceptionally high, as these ions are transferred along a series of hydrogen bonded water molecules by rearrangement of hydrogen bonds [10]. This means that  $\text{OH}^-$  will be a major carrier of charge during the desalination and can eventually when pH continuously increase suppress the transport of the target anions as it has been seen during electrochemical extraction of  $\text{Cl}^-$  from concrete [11]. Further such high pH may damage the material.

Compared to the reference experiment (XIX-a) the average pH of the tile segments (XIX-b to XIX-e) increased from 9.6 to between 9.9 and 10.4 (Table 2). As there is no reference experiment for the XVIII tiles the initial pH is not known, but an increase from 8.8 in the shortest experiment to 9.2 in the longest is seen, indicating that also in these tiles the average pH increased with the duration.

### 3.5 Chloride removal from spiked XIX tiles

The Cl concentration of the anode poultice was between 2,540 and 2,740 mg/kg in experiments XIX-b to d and 1,140 mg/kg in experiment XIX-e. The concentration in the cathode poultice was less than 62 mg/kg in all these experiments. This underlines that electromigration was the major transport mechanism for  $\text{Cl}^-$  removal in these experiments.

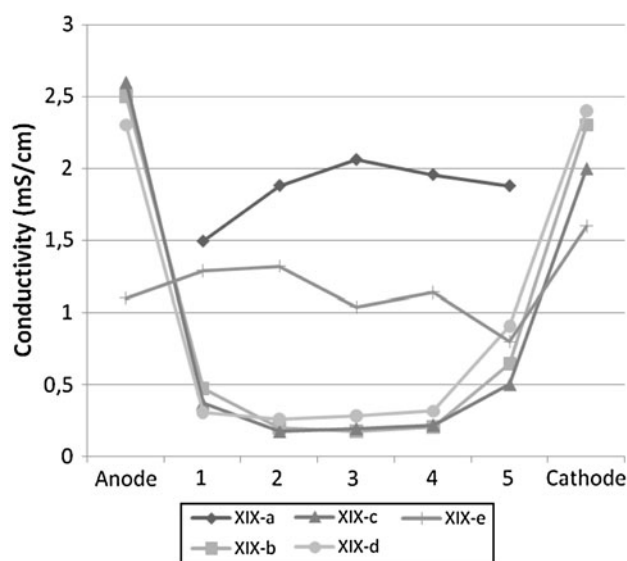
Profiles of Cl concentrations in the tile segments at the end of experiments XIX-a to e are shown in Fig. 6 together with the upper and lower threshold values of the Önorm B 3355-1. The Cl concentration of the reference tile (XIX-a) was relatively stable and exceeded the upper threshold value. In experiments XIX-b to d the concentration was



**Fig. 6** Concentration profiles in the tile segment after the electrokinetic experiments (XIX-b to e) in comparison to the reference experiment (XIX-a) where no current was applied and the upper and lower limits of the ÖNORM B 3355-1 (1 closest to the anode and 5 closest to the cathode)

well below the lower limit all through the tile segments and thus the electrokinetic desalination was successful when treating these spiked tiles. An almost complete desalination was probably the cause for the sharp increase in resistivity (seen as increase in voltage at Fig. 4a, b) as was found in all these three experiments. Experiment XIX-e, which was stopped after 2 days and before the expected increase in voltage (Fig. 4b), still had chloride in all pieces, even though the concentration was low closest to the anode (below the lower threshold value).

To evaluate if the sharp increase in resistivity can be linked directly to an almost complete desalination of the tile or if the cause it to be found elsewhere, the conductivities measured in extractions of the tile pieces and the poultice are shown in Fig. 7. At first it is noticed that the conductivity in the poultice at both ends is very high and of approximately the same size in experiments XIX-b to d, and it is even higher than in the tile pieces of the reference tile (XIX-a). The high conductivity at the anode is caused by the high  $\text{Cl}^-$  concentration and also dissolution of carbonates due to the acidification is increasing the conductivity. Formation of  $\text{CaCl}_2$  in the anode poultice is possible, but as this salt is easy soluble it is dissolved in the extractions made for analysis and included in both the measurements of chloride and conductivity. In the cathode poultice the high conductivity is expected mainly linked to a high  $\text{OH}^-$  concentration from electrolysis of water at the cathode. It is seen from Fig. 7 that the transport of  $\text{OH}^-$  into the tile is somewhat hindered, as there is a much lower



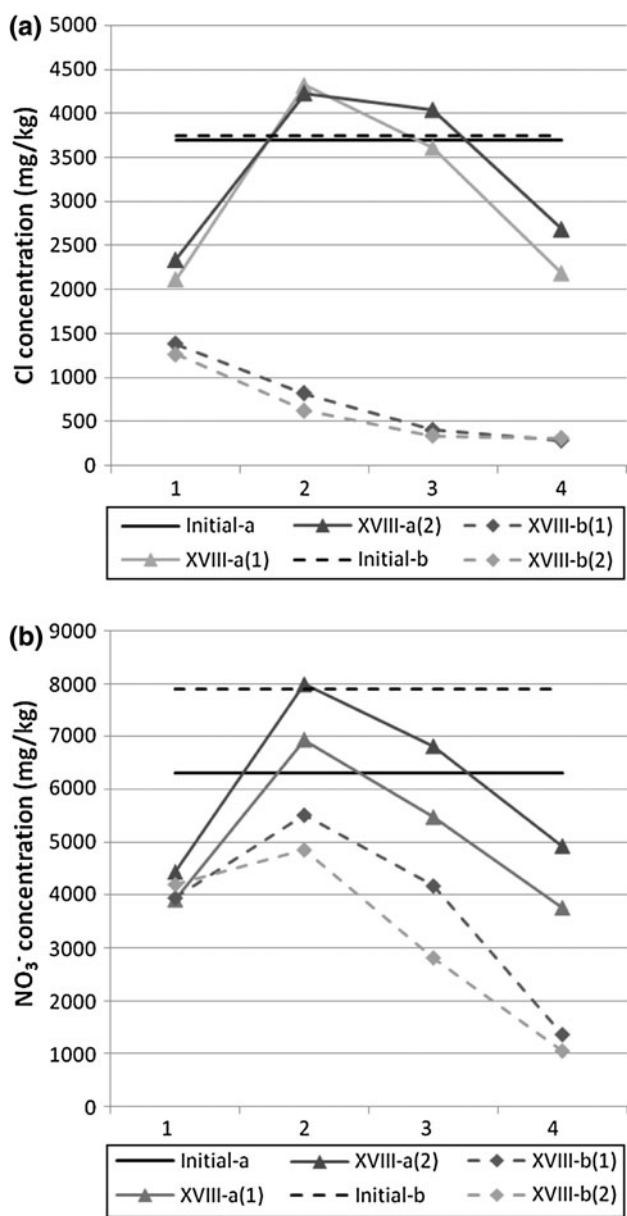
**Fig. 7** Conductivity in the poultices and tile pieces (measured in suspensions) at the end of experiments XIX-a to e

conductivity in the tile piece next to the cathode than in the cathode poultice. In the carbonate rich poultice the reaction  $\text{CaCO}_3 + 2\text{OH}^- \rightarrow \text{Ca(OH)}_2 + \text{CO}_3^{2-}$  takes place. This reaction is immobilizing a part of  $\text{OH}^-$  for electromigration. The transformation of  $\text{CaCO}_3$  to  $\text{Ca(OH)}_2$  is the reaction that is utilized in electrochemical realkalization of concrete [3]. The  $\text{CO}_3^{2-}$  ion is unwanted in the tile as this ion together with e.g.  $\text{Na}^+$  can form a new salt decay problem. Since the conductivity in the tile is low at the end of the experiments XIX-b to d it is expected that  $\text{CO}_3^{2-}$  have precipitated with the arriving  $\text{Na}^+$  in the poultice ( $\text{Na}_2\text{CO}_3$  is soluble and is included in the conductivity measurement). The conductivity in piece 5 closest to the cathode is higher than in the central part of the tile, and future research involve an investigation of the chemical reactions in the zone next to the poultices. Overall, Figs. 6 and 7 show that desalination is successful in the spiked tile segments.

### 3.6 $\text{Cl}^-$ , $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ removal from XVIII-century tiles

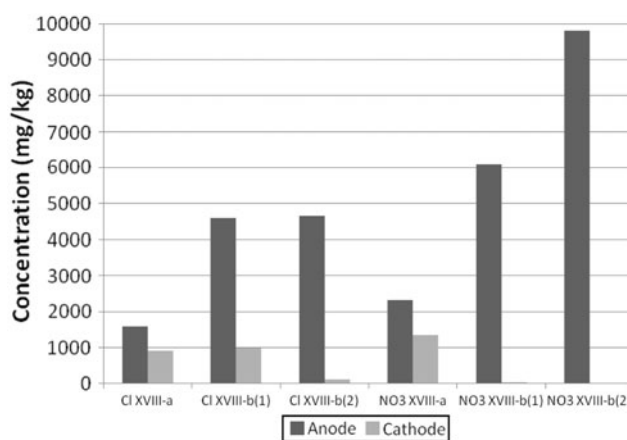
The concentration profiles of  $\text{Cl}^-$  and  $\text{NO}_3^-$  at the end of the electrokinetic desalination experiments with XVIII-century tiles are shown in Fig. 8a and b, respectively, and the concentrations in the poultice are shown in Fig. 9. On basis of the final content of the anions in the tile pieces and poultices, an approximation of the initial concentrations in the two tiles was made. As some of the  $\text{Cl}^-$  will form  $\text{Cl}_2$  gas and thus leave the cell, the real initial chloride concentration was most likely higher than the calculated. In all the three of the experiments XIX-b to d the mass balance





**Fig. 8** Concentration profiles in the XVIII-century tiles at the end of the electrokinetic desalination experiments **a** Cl<sup>-</sup> and **b** NO<sub>3</sub><sup>-</sup> (the initial concentrations are calculated on basis of the total amount of the ions removed and left in the tiles after treatment (1) and (2) refer to the two profiles made for each tile parallel to the electric field. Slice 1 was closest to the anode

for Cl<sup>-</sup> was about 70% showing that about 30% of the total initial Cl amount had taken part in the anode process. Thus the approximated initial Cl<sup>-</sup> concentration is expected to be significantly higher than shown in Fig. 8a. The approximated initial Cl<sup>-</sup> concentration was almost the same in the two XVIII tiles (about 3,700 mg/kg), whereas the NO<sub>3</sub><sup>-</sup> concentration varied more (from 6,300 mg/kg in tile XVIII-a to 7,900 mg/kg in tile XVIII-b). As the duration of experiment XVIII-b was longer than for experiment



**Fig. 9** Concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in the poultice at the electrodes in the two experiments XVIII-a and XVIII-b (sample XVIII-b(1) is the concentrations in the poultice that was removed after 7 days and XVIII-b(2) in the poultices at the end of experiment)

XVIII-a it is also expected, that more Cl<sup>-</sup> took part in the anode process and thus the initial concentration in tile XVIII-b was probably even higher than in tile XVIII-a. The initial concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> far exceeded the upper threshold values of the Önorm B 3355-1.

The concentration of SO<sub>4</sub><sup>2-</sup> was very low (average 14 mg/kg) in tile XVIII-b and no SO<sub>4</sub><sup>2-</sup> was found in the poultice at the end of the experiment. The SO<sub>4</sub><sup>2-</sup> was also higher in tile XVIII-b and the approximated initial concentration was 135 mg/kg. Even though this concentration is much lower than the concentration of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> and the concentration is far below the lower limiting value of the Önorm B 3355-1 the sulphates cannot automatically be neglected as damaging, as the values in the Önorm B 3355-1 are based on presence of single salts. Actual threshold values are different for mixed salts than for single salts [12], but threshold values for mixed salts have not yet been defined, and thus the threshold values for single salts from then Önorm B 3355-1 are used for the evaluation in the present paper. Prediction of the behaviour of mixed salts is complex due to formation of double salts as e.g. Na<sub>3</sub>NO<sub>3</sub>SO<sub>4</sub>·H<sub>2</sub>O (darapskite) as was observed experimentally by De Clercq [12] in a limestone.

Tile XVIII-b had higher concentration of all three anions than tile XVIII-b and had also the most damaged glazing of the two tiles.

From Fig. 8a and b it is seen that the charge transfer of experiment XVIII-a (about 3,000 C) was far too low for a sufficient desalination. The concentration profiles for Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> have similar shapes with lower concentrations closest to the electrodes, and from Fig. 9 it can also be seen that a relatively high concentration of both ions were found in the poultice at both ends. The concentrations were higher in the anode poultice as expected as

electromigration is an important transport mechanism in this system, but the relatively high concentration in the cathode poultice shows that in this system, also diffusion plays an important role in the beginning of the treatment of tiles with such high concentrations.

In experiment XVIII-b the charge transfer was about 21,700 C, which was still not sufficient for a complete desalination as seen from Fig. 8a and b, though the concentrations of both anions were decreased significantly. The conductivity in tile XVIII-b was also much lower than in tile XVIII-a indicating a well progressing desalination (Fig. 10). The lower threshold value for chloride was just obtained in the pieces closest to the cathode, but the rest of the tile had too high concentration. The lower threshold value for  $\text{NO}_3^-$  was not met in any of the tile pieces.

In the experiments here it seems as the removal of  $\text{Cl}^-$  is faster than removal of  $\text{NO}_3^-$ . This can be related to the lower ionic mobility of  $\text{NO}_3^-$  ( $5.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ) compared to  $\text{Cl}^-$  ( $7.9 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ) and it can be related to a possible lower solubility of the present nitrate-salts or a combination of the two. From previous work with desalination of a single brick spiked with  $\text{Ca}(\text{NO}_3)_2$  successful  $\text{NO}_3^-$  removal was obtained [13] and also in a pilot scale experiment on a salt contaminated masonry the removal of  $\text{NO}_3^-$  was successful. Thus it is expected that also from the tile more  $\text{NO}_3^-$  could have been removed if more charge had been passed through.

The removal percentages in experiment XVIII-b (calculated on basis of the approximated initial values) were:

- >81%  $\text{Cl}^-$
- ~59%  $\text{NO}_3^-$
- ~22%  $\text{SO}_4^{2-}$

The desalination process is thus well progressing, even though it has not been completed.

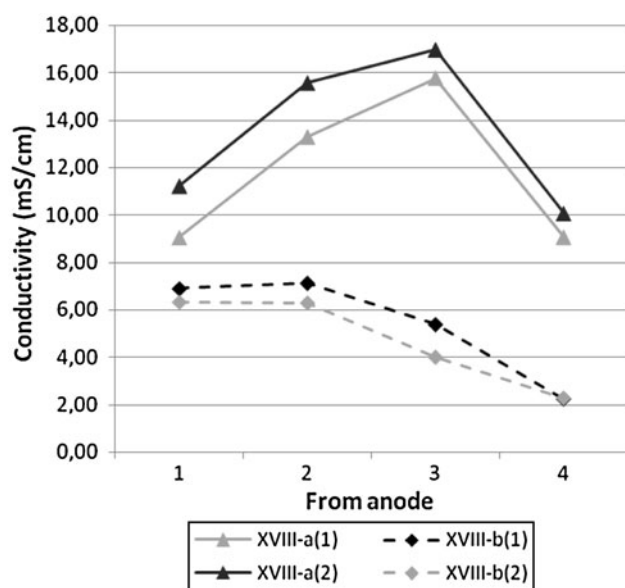
## 4 Conclusions

Electrokinetic desalination of a model system with a single tile contaminated with a single salt (NaCl) showed clearly that the overall principle of the method works since the initial high and problematic concentration of about 1,340 mg  $\text{Cl}^-/\text{kg}$  was reduced to a very low and unproblematic concentration (<20 mg/kg) within few days of applied current. The overall conductivity in the tile at the end of the desalination experiments was low, indicating that the major ionic transport by electromigration had been out from the tile. At low ionic concentration, electroosmosis was seen in the tile from anode towards cathode. Treatment of an original XVIII-century, severely salt contaminated tile showed promising results with removal percentages of >81%  $\text{Cl}^-$ , ~59%  $\text{NO}_3^-$  and ~22%  $\text{SO}_4^{2-}$ , even though full desalination was not obtained. Probably the charge transfer was insufficient and should be increased to increase the removal percentages. In the original tile, the removal of  $\text{Cl}^-$  was faster than  $\text{NO}_3^-$  which corresponds to a lower ionic mobility of  $\text{NO}_3^-$ .

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**Fig. 10** Profiles of conductivities in the XVIII-century tiles at the end of the electrokinetic experiments. (1) and (2) refer to the two pieces in which the tiles were separated parallel to the electric field at the end of the experiments (1 closest to the anode and 5 closest to the cathode)

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