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Salt Weathering on Buildings and Stone Sculptures

Editors:
I. Ioannou & M. Theodoridou

EDITORS:

Ioannis Ioannou, PhD
University of Cyprus
Department of Civil and Environmental Engineering
Building Materials & Ledra Laboratories
PO Box 20537
1678 Nicosia
Cyprus
ioannis@ucy.ac.cy

Magdalini Theodoridou, PhD
University of Cyprus
Department of Civil and Environmental Engineering
Building Materials & Ledra Laboratories
PO Box 20537
1678 Nicosia
Cyprus
mtheodo@ucy.ac.cy

Electrochemical Desalination of Historic Portuguese Tiles, Azulejos, in laboratory scale

Ottosen L.M.^{1*}, Ferreira C.² and Christensen I.V.¹

¹ Dept. of Civil Engineering, B118, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

² CERNAS, Escola Superior Agrária, Coimbra, Portugal

*corresponding author's email: lo@byg.dtu.dk

ABSTRACT

Soluble salts causes decay of historic Portuguese tiles. Treatment options for removal of the salts are few. The present paper deals with development of a method for electrokinetic desalination, where an electric DC field is applied. Experiments are conducted with XVIII century tiles with and without mortar from the tile bed. The focus is on removal of salts over interphases between glaze/biscuit and biscuit/mortar. As received, the tiles had NaCl crystals under loosened glaze, whereas after treatment no salt crystals were found (by SEM-EDX). Desalination of the mortar occurred before biscuit desalination as little chloride and nitrate was removed from the latter, whereas the concentrations were significantly reduced in the mortar. This might be linked to the interface between biscuit and mortar, where poor contact and cracks with air could be the reason (the mortar was very loose), hindering the current in passing. This is a point for further investigation.

Keywords: Azulejos, tiles, chlorides, nitrates, electrokinetic desalination

1 INTRODUCTION

Ceramic tiles, *azulejos*, are very important to Portuguese culture. They have been used during five centuries. Thousands upon thousands of tiles have been produced and applied as panels in both the interiors and the exteriors of private and public buildings as well as in the covering of whole facades (Pessoa et al. 1996). The tiles are placed on the wall in a tile bed of mortar. The Portuguese tiles applied in panels are designed for surface continuity, so the width of joints does not interfere with the image. Their sides are beveled and, when mounted together to form a panel, their edges contact (Mimoso et al. 2009). This may constitute a problem in cases the tiles are wet for a longer period causing swelling and subsequent cracked and damaged glazing.

Soluble salts are a major cause of azulejo decay and, aside from human actions, are likely to be the most important cause of decay and loss of single tiles as well as whole panels (Mimoso et al. 2009). The salts can enter the tiles from rising groundwater in the wall to which they are attached. Rain water may also be introduced through the roofs of ancient buildings (Borges et al 1997). Mimoso et al (2009) visited different monuments around Portugal aiming to assess decay patterns, particularly when caused by salt crystallization. They concluded that the durability depends largely of the tile being defect-free and mounted on essentially dry walls. Tiles with manufacturing defects may have their glaze partially cracked or delaminated, thus offering easy routes for moisture propagation and salt crystallization.

Treatment options for salt damaged tile panels are few. If possible without damaging the tiles, they can be removed from their support and treated separately. Before the removal lifted glaze is consolidated by gluing an inert material to the surface. One difficulty encountered in the removal can be hard mortars and/or cement rich mortars in tile bed and filling the joints. After removal, the mortar on the back of the tile is removed with spatula and scalpel. Finally, removal of soluble salts entails submerging the tiles in distilled water (Gomes & Monteiro, 1996). The desalination during soaking is followed by conductometric measurements or determination with ion chromatography (Pessoa et al. 1996). Electrochemical desalination of single azulejo tiles has previously been reported (Ottosen et al. 2010). Model tiles (XIX century) spiked with NaCl in the laboratory were desalinated successfully as the Cl concentration was lowered from about 0.13 wt% Cl to less than 0.01 wt% all through the tile. Desalination of two salt infected tiles from Centeno Palace, Lisbon, was also tested. The charge transfer in these experiments was too low to obtain full desalination, but significant decreases were seen: >81% Cl, ~59% NO₃⁻ and ~22% SO₄²⁻. The present paper reports a further investigation of electrokinetic desalination of tiles from Centeno Palace focusing on the interfaces between glazing-biscuit and biscuit-mortar.

2 ELECTROKINETIC DESALINATION OF TILE – THE PRINCIPLE

Removal of fragile tiles followed by soaking can increase the damage. Electrokinetic in-situ desalination could be less harsh treatment method, as the salt extraction can be done by placing electrodes around the salt damaged area, i.e. the fragile tiles are not touched. Electrokinetic desalination is based on application of an electric DC field to a moist, porous and salt infected building material. In the moist pores the electric current is carried by ions (electromigration). The positive ions will move towards the negative electrode and the negative ions towards the positive electrode. During the process, the concentration of ions from the salts will decrease in the porous material as the ions concentrate in a poultice around the electrodes (Ottosen & Rørig-Dalgaard, 2009). The overall principle and laboratory setup for of electrokinetic salt extraction from a single tile is shown in figure 1. The tile is placed with the glazing down and two frames with clay poultice (Rørig-Dalgaard & Ottosen, 2009) are placed as shown. On top of the clay poultice the metallic electrodes are placed and the electrodes are connected to a power supply.

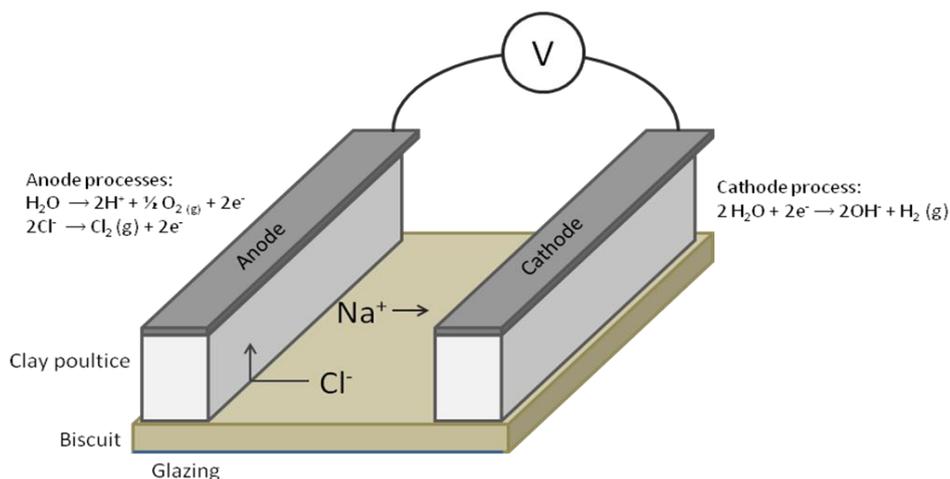


Figure 1. Laboratory setup and principle in electrokinetic desalination of single tiles.

In metal electrodes the electric current is carried by electrons and in the pore water it is carried by ions. The processes that transform current carried by electrons to current carried by ions and vice versa are 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. At figure 1, the prevailing electrode processes during tile desalination are given. At both electrodes there

are pH changes. The pH increases at the cathode and decreases at the anode. The clay poultice must hinder these pH changes in reaching the tile. Further the clay poultice ensures good electrical contact between metallic electrode and tile and the clay serves as sink for removed ions. When the clay poultices are removed, the ions of the salts are removed with it.

3 MATERIALS AND METHODS

3.1 Tiles for the experiments

Two XVIII century tiles from Palacio Centeno, Lisbon were used in this investigation (figure 2). The tiles were removed from the site during a renovation and conservation action. They were part of tile panels, which suffered from salt decay. The panels were removed tile by tile for desalination by submersion, but due to the poor condition of some of the tiles (of which the tiles in figure 2 are examples), it was decided not to use them again and they were not desalinated. The original dimensions of the tiles were 14 x 14 x 1.5 cm. Tile (A) was loosened from the mortar on the back, whereas tile (B) still had a layer of up to 1.5 cm thick mortar. The mortar sticking to tile B was brownish, sandy and with larger white grains. The mortar has a loose structure and it may be original. It does not contain cement.

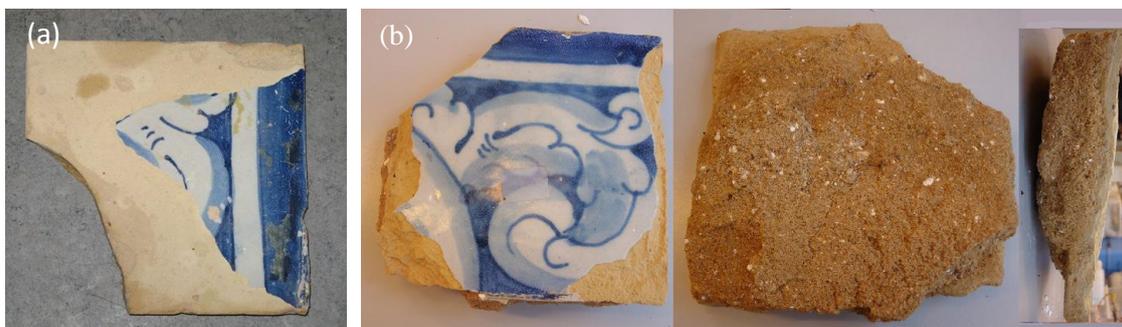


Figure 2. The two salt damaged tiles used in the experimental work. (a) One corner of the biscuit is missing and severe loss of glazing, and (b) Also missing a corner. Tile B is shown from the front, the back (where mortar is attached) and from the side.

From tile B a sample from the biscuit and one from the mortar was taken prior to the desalination experiment. The biscuit sample was taken at places without mortar (few small samples taken from around the edge (in total 12.3 g) and mortar was carefully scratched off also around the sample (in total 14.1 g). No samples were taken prior to desalination experiment A.

3.2 Experimental setup and procedure

The tiles had dried at room temperature and were wetted by spraying distilled water on the back side (opposite to the glazing). Little water was sprayed on the tile and it was left in a plastic bag for some days. The procedure was repeated until the suction of water into the biscuit was very slow. This procedure was chosen rather than soaking because soaking could mean wash off efflorescence or surface near salt crystals. Further one question to be answered from the investigation was if electrokinetic extraction could be performed without soaking to protect the tile, which can be a tough treatment in case of disintegrated glaze.

The tiles for the desalination experiments were wrapped in plastic film to hinder evaporation in the dry laboratory atmosphere. The tiles were placed with the glazing down. Two rectangular holes were cut in the upper side of the plastic film for the electrodes. A rectangular plastic frame covering the full length of the tile was placed over the hole (for both tiles the frame for the anode was shorter than that for the cathode due to the missing corners of the tiles). Poultice of

kaolin clay and CaCO_3 (Rörig-Dalgaard & Ottosen, 2009) 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 subsequently connected to the power supply. Figure 1 shows the experimental setup.

3.3 Electrokinetic desalination experiments performed

This investigation includes two desalination experiments. Table 2 shows characteristics of the two experiments. The dry weight for tile A is the weight of the air dried tile. The dry weight of tile B is separated into tile and mortar, which is done on basis of the segments by the end of the experiment (after drying at 105°C). The dry weight of the two biscuits is similar. The water content (water/dry matter) after spraying water shown for experiment A is based on the dry weight obtained at room temperature so the actual water content might be higher. For tile B the water content from the two initial samples are shown. Finally, current range, voltage range and duration of the experiments are shown.

Table 1. The two electrokinetic desalination experiments. (*calculated on basis of air dried tile, for tile B the T indicates tile and M mortar)

Exp.	Dry weight (g)	Water content (wt%)	Current (mA)	Voltage range (V)	Duration (d)	Charge transfer (C)
A	389	4.4*	5	5-74	55	23,800
B	T 359/M 316	T 12.0/M 14.3	5-10-20	2-32	23	34,900

The power supply was set to supply a constant current during the experiments. All through experiment A the current was 5.0 mA. Experiment B also started at 5 mA, but after 3 days the current was increased to 10 mA, and after additionally 3 days the current was increased to 20 mA, which was kept for the remaining 17 days of the experiment. During the experiments voltage and current were measured approximately every 24 hours. During the first 46 days there was no interference of experiment A, but the clay was changed after 46 and 53 days. Every day, the last 9 days of experiment A little water was sprayed to the back of the tile. In experiment B the clay was changed after 7, 10, 13, 16 and 19 days. Water content, pH and concentrations of Cl^- and NO_3^- were measured in the removed clay.

At the end of the experiments the tiles and mortar were segmented with hammer and chisel (8 segments each). The tile was first broken into two pieces running from anode towards cathode (I and II). The two pieces were subsequently separated into 4 segments each. Segment 1I and 1II had been covered by the anode poultice, segments 2 and 3 had been between the electrodes, and finally segment 4I and 4II had been covered by cathode poultice during the experiment. For tile B a third segment was made from the biscuit at the cathode side (segment III). This segment had not been covered with neither mortar and nor cathode poultice.

3.4 Analytical

After segmentation each tile piece and the clay poultice were weighed, dried at 105°C for 24 hours and weighed again for calculation of water content (water/dry matter). The dried pieces were powdered by hand in a mortar. Extractions in distilled water (10 g powder in 25 ml) were made. After 24 hours 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^- , NO_3^- and SO_4^{2-} were measured by ion chromatography and Na by AAS. SEM-EDX and light microscope were used to investigate the salt damage. Small pieces of disintegrated glaze was removed from the tile and investigated in the SEM-EDX with the glaze down to see if salts had precipitated here. The investigation was made both before and after electrokinetic desalination.

4 RESULTS

4.1 Salt damage of the experimental tiles

It is seen that the glazing in general is lost from the outer edges of the experimental tiles (figure 2), which is a common pattern when tiles are salt contaminated (Mimoso et al. 2009). The edges of the tiles in panels meet and the forces developed due to expansion under long periods with wet conditions make the glazing loose adherence. Figure 3 shows a typical pattern at the edge of the glazing of the experimental tiles, where the glazing is cracked and disintegrated in flakes.

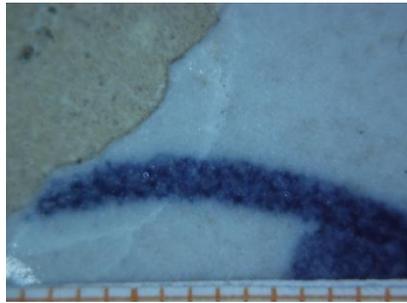


Figure 3. Disintegrated glaze from experimental tile. (Length of foto corresponds to 15 mm)

When removing such loosened flakes and investigating the surface opposite to the glazing in SEM, salt crystals are seen (figure 4 is an example). Elemental mapping (SEM-EDX) reveals that these crystals are NaCl. Nitrogen was not found under the glaze in these investigations even though the concentration of nitrate was very high (see later). In figure 4 is also shown the elemental mapping for oxygen and silicon, which were most abundant around the salt crystals. The salts are probably worsening the disintegration of the glaze, but whether the crystallization happened after the disintegration or before cannot be concluded from this investigation.

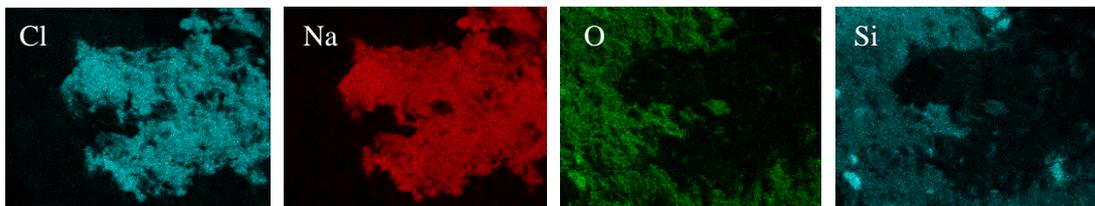
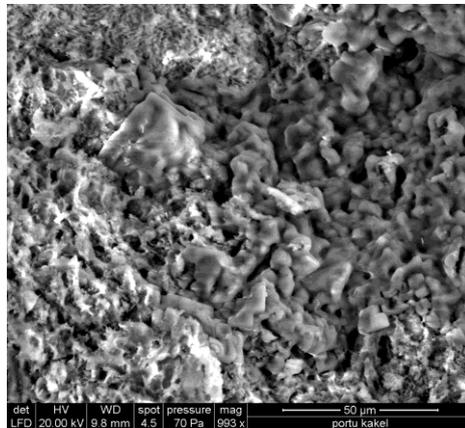


Figure 4. Example of SEM-EDX investigation of the back side of lifted glaze from tile A. The elemental mapping reveals that the salt crystals are NaCl and under the NaCl is mainly quartz grains (SiO_2) probably from the biscuit as the back side is colored as the biscuit.

4.2 Desalination of single tile

The initial concentration of salt in tile A was not measured, as the analytical methods used are destructive. The average initial concentrations were instead calculated on basis of the analysis made by the end of the experiment (material weight and concentrations in clay poultice and tile). The calculated average initial concentrations were: 0.69 wt% Cl^- , 1.77 wt% NO_3^- , and 0.024 wt% SO_4^{2-} (the concentration of Cl^- has actually been slightly higher as the part which had entered in the electrode process was left out from the calculation as it is an unknown factor). The concentrations of Cl^- and NO_3^- were very high compared to the limiting concentrations given in the Austrian Önorm B 3355-1, as the concentrations far exceeds the highest value active salt removal is advised (0.1 wt% Cl^- , 0.15 wt% NO_3^- , and 0.25 wt% SO_4^{2-}).

Figure 5 shows the concentration profiles of Cl^- and NO_3^- in tile A by the end of the desalination experiment. The profile in each side of the tile (I and II from the segmentation) can be seen, so can the calculated average initial concentrations. There is a very good agreement between the profiles A and B indicating that the possible concentration variations between the two sides were leveled out during the treatment. The desalination was not completed as the concentrations of especially NO_3^- still were very high. During the experiment about 87%, Cl^- , 62% NO_3^- , and 20 wt% SO_4^{2-} were removed from the tile, and it corresponds to the removed percentages from (Ottosen et al. 2010) even though the concentrations in the present tile were significantly higher. Additional experiments are ongoing to investigate if higher removal percentages can be obtained with this setup. The shape of the NO_3^- profile (with the lowest concentrations under the electrodes) is similar to the obtained in (Ottosen et al. 2010) and it indicates that the removal is faster below the electrodes than between. This may be linked to higher water content under the clay poultice during the experiment, but the water content of all tile segments was between 9% and 12 % by the end of the experiment (lowest under the cathode and highest under the anode) and thus the influence from the water content cannot be confirmed. The final concentration of nitrate was though below the average initial concentration all through the tile.

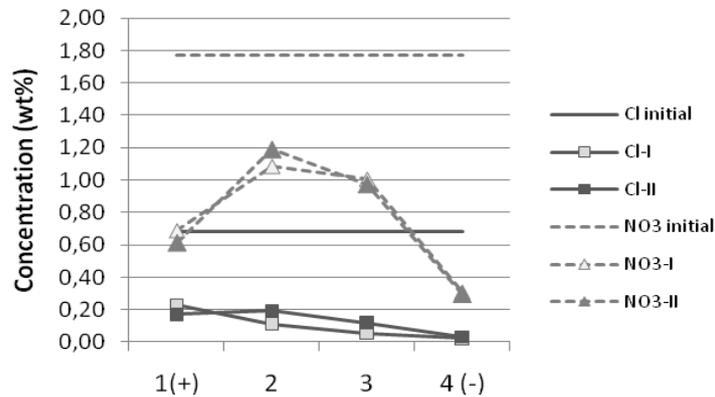


Figure 5. Concentration profiles of Cl^- and NO_3^- in tile A by the end of the electrokinetic desalination experiment. Calculated average initial concentrations are given. Profile I and II refers to the segmentation.

Several small pieces of lifted glazing was removed and investigated upside-down by SEM-EDX after the experiment, and only one piece showed traces of Na. In neither of the pieces Cl was identified. Thus the salts precipitated under the glaze was removed during the desalination experiment. This is important to the further development of the method as it is considered of utmost importance to remove the salts precipitated here to stop the salt damage.

4.3 Desalination of tile and mortar

Some characteristics of the reference pieces of mortar and biscuit from tile B taken prior to the desalination experiment is seen in table 2. The concentrations of chloride and nitrate are very high in both tile and biscuit and it is necessary to desalinate both. The concentrations in the tile B itself are very similar to the concentrations in tile A.

Table 2. Concentrations in a small piece of mortar and biscuit from tile B before electrokinetic treatment

	Cl (wt%)	NO ₃ (wt%)	SO ₄ (wt%)	pH	Water content (%)
Mortar	0.67	1.39	0.006	8.9	14.3
Biscuit	0.79	1.70	0.035	8.2	12.0

Figures 6a and 6b show the concentration profiles of Cl⁻ and NO₃⁻ in tile and biscuit by the end of experiment B. The concentrations from table 2 are here used as initial concentrations. The mass balances (initial amount in tile/final amount in tile and clay) based on these concentrations are Cl⁻ 103% and NO₃⁻ 137%, which indicates that the Cl concentrations in table 2 are representative to the tile and mortar, whereas the NO₃⁻ concentration is too high either in the tile or in the mortar compared to the average concentrations. It is clearly seen from figure 6 that the concentrations of both anions were decreased significantly in the mortar, whereas less removal had occurred from the tile itself. In average probably no nitrate was removed from the tile, whereas a decrease in chloride was seen. When comparing the profiles in tile B (figure 6) to the profiles in tile A (figure 5) it is noticed that the concentrations in the two sides of the tile (made during the segmentation) differs much more in tile B. The reason can be air-filled cracks between mortar and biscuit, where the current cannot pass, but it can also reflect variations in initial concentrations, which had not been leveled out.

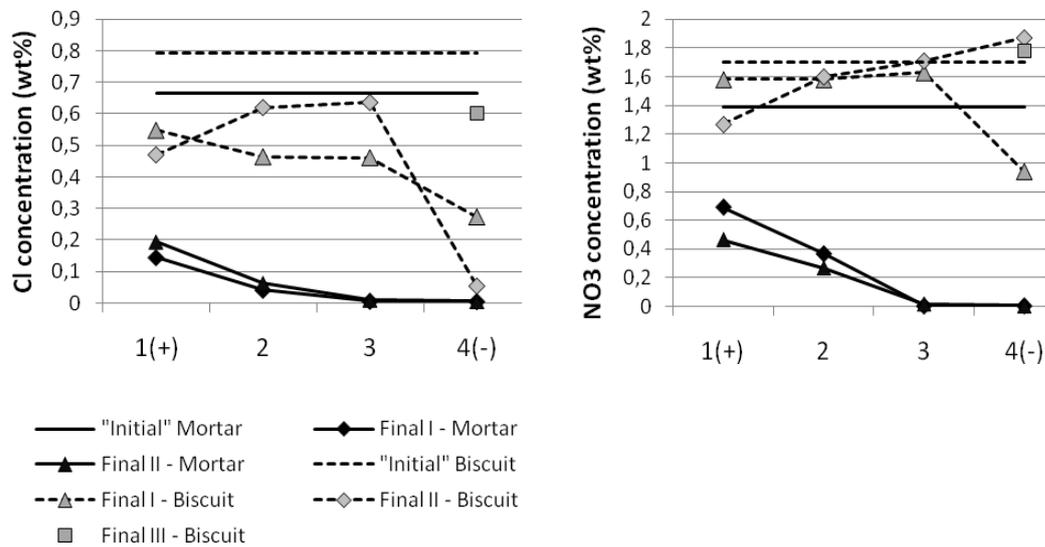


Figure 6. Concentration profiles in tile and mortar (tile B) by the end of the experiment. The initial concentrations indicated corresponds to the concentrations in the small initial samples taken.

Figure 7 shows the amount (in mole) of the two ions removed towards cathode and anode (based on the analysis of the concentrations in the clays, when this was replaced). During the first period it is seen that both anions were transported towards the cathode by diffusion (or advection) but during the remaining time of the experiment this transport was very limited. Figure 7 also shows that electromigration of Cl⁻ occurs from the beginning of the experiment,

whereas the electromigration of nitrate starts after a charge transfer of approximately 10.000 C (corresponds to 10 days). The ionic mobility of Cl^- is little higher than that of NO_3^- , but this cannot be the major cause. One reason can be less solubility of the nitrate salts, but this is not yet confirmed. Positive to the further development is it that the removed amount of both ions was still increasing when the experiment was finished, revealing that better removal percentages could have been obtained if the experiment was continued. Future experiments will show if sufficient desalination of the biscuit can be reached, when the electrodes are placed on the mortar. Electric current flows where the conductivity is highest, and when the mortar is desalinated, it is expected that desalination of the biscuit is next. This investigation is a step towards electrokinetic desalination of tile panels. It underlined that focus must be laid on mapping interfaces between biscuit and mortar behind. If the tile is only loosely held by the mortar, the current may bypass the biscuit. The investigation showed that it is possible to remove the salts crystallized under the lifted glaze.

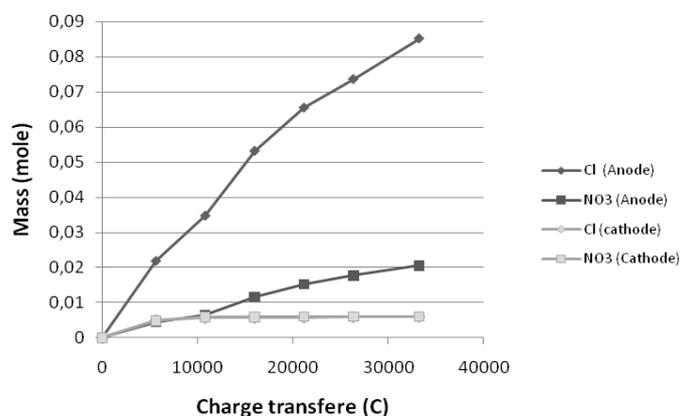


Figure 7. Removed mass (in mole) of chloride and nitrate into the clay poultice at the anode and cahtode during experiment B as a function of charge passed through the system

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