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Electrochemical desalination of historic Portuguese tiles – removal of chlorides, nitrates and sulfates

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ABSTRACT

Soluble salts cause severe decay of historic Portuguese tiles. Treatment options for removal of the salts to stop the decay are few. The present paper deals with development of a method for electrochemical desalination, where an electric DC field is applied to the tiles. Laboratory experiments were conducted with single XVIII tiles from Palácio Centeno, Lisbon, Portugal. Large parts of the glaze and parts of the biscuit were lost from salt decay. The major aim of the investigation was to see if the method could offer sufficient salt removal in the biscuit and in the
interface between biscuit and glaze, where salt crystals were clearly identified by SEM-EDX before desalination. The concentrations of chloride and especially nitrate were very high in the tiles (around 280 m mol Cl⁻/kg and 450 m mol NO₃⁻/kg respectively). Both anions were successfully removed to below 6 m mol/kg during the electrochemical treatment. The removal rate was similar for the two anions so the chloride concentration reached the lowest concentration level first. At this point the electric resistance increased, but the removal of nitrate continued unaffected till similar low concentration. The sulfate concentration was initially very low, but never the less sulfate removal started at the point where chloride and nitrate concentrations were very low in the tiles. Investigating the interface between biscuit and glaze after the treatment showed no signs of crystallized salts, so also in this important point, the desalination was successful. Based on the obtained results an important step is taken towards development of an electrochemical technique for desalination of tile panels.

Keywords: Azulejos/tiles/electrokinetic/desalination/nitrates/chlorides/salt decay
1. Research aims

Glazed ceramic tiles (Azulejos) are an important part of the Portuguese heritage. Presence of soluble salts causes decay and irreversible loss of tile panels, but there are no efficient in-situ desalination techniques available. This paper investigates the possibility for desalinating single tiles by application of an electric DC field (electrochemical desalination). The experimental tiles are salt damaged XVIII century tiles from Palácio Centeno, Lisbon, Portugal with high concentrations of chloride and nitrate. In addition to investigating the removal of the salts from the biscuit, special emphasis is laid on removal of salts from the interface between biscuit and glaze as salts here causes disintegration of the glaze. The sulfate concentration was low initially, but never the less the sulfate removal was followed, as even low sulfate concentrations may cause salt damage. In case of successful desalination of a single tile (inclusive interface between biscuit and glaze) by the electrochemical technique, the first important step is taken towards development of a new in-situ method for desalination of tile panels.

2. Introduction

Ceramic tiles (Azulejo) are an important part of the Portuguese cultural heritage. Actually, in Portugal, tiles have been used in the decoration of buildings since the 15th century. The tiles are vulnerable to salt decay as salts may crystallize in the interface under the glaze causing detachment [1]. The salts enter the tiles from
rising groundwater, sea spray or penetrating rain water through roofs of ancient buildings [1]. Soluble salts are a major cause of tiles decay and, aside from human actions, are likely to be the most important cause of decay and loss of single tiles and whole panels [2].

At present options for desalination of tile panels are few. Conservation actions follow one of two approaches: either poultice materials are used to treat tile panels in-situ i.e. wet adhesive pastes are applied to the surface in order to draw out the soluble salts by advection and diffusion or if possible without physically damaging the tiles, they can be removed from their support and treated one by one by submersion in distilled water [3]. The desalination during soaking can be followed by conductometric measurements or determination with ion chromatography [1].

Electrochemical desalination of tiles is a new option presently investigated. This work is focused on electrochemical desalination of single tiles. Salts from both biscuit and interface between biscuit and glaze must be removed to have an efficient conservation technique. If so, the next step towards developing the technique for tile panels will be testing on the whole system with wall, mortar bed and tile. It is important to remove salts from all parts. Otherwise the tiles will soon be salt infected again from salts entering from mortar and wall.
Electrochemical desalination of single azulejo tiles was tested in laboratory for model tiles (XIX century) spiked with NaCl [4]. Successful desalination was obtained as the Cl⁻ concentration was lowered from 0.13 wt% Cl⁻ to less than 0.01 wt% [4]. Electrochemical desalination of salt infected tiles from Centeno Palace, Lisbon, has also been tested [4, 5], but here the charge transfer was too low to obtain full desalination; the decreases obtained were >81% Cl⁻, ~59% NO₃⁻ and ~22% SO₄²⁻ [4]. Electrochemical desalination of other matrices has also recently been tested: baked clay bricks [6-10], sandstones [11-13] and granite [14]. These studies have mainly focused on electrochemical desalination of single stones representing somewhat homogeneous matrices, but in relation to tiles, the salt crystallization under the glaze is of major concern. The present paper reports a further investigation of electrochemical desalination of tiles from Centeno Palace focusing on obtaining full desalination. The removal rate of Cl⁻ and NO₃⁻ will be followed to investigate the possible differences. Special emphasis is on the desalination of the important interface between biscuit and glaze.

2.1 The principle of electrochemical desalination

During electrochemical desalination electrodes are placed externally on the surface of the salt infected material. Figure 1 shows the setup and principle for electrochemical desalination of a tile. At both electrodes there are pH changes due to electrolysis reactions:
At the anode: \[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 (g) + 2e^- \]  \hspace{1cm} (1)

At the cathode: \[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 (g) \] \hspace{1cm} (2)

As seen from (1) and (2) pH decreases at the anode and increases at the cathode. It is necessary to neutralize the pH changes to prevent severe pH changes in the tile. Hendrix et al. 2011 [12] underlined how important it is to avoid the acidification, as in experiments without pH neutralization; the experimental stones were severely damaged close to the anode. Also in order to obtain sufficient desalination pH neutralization can be crucial. Kamran et al. 2012 [9] showed that without neutralization at the electrodes, the desalination process in bricks stopped due to formation of a sharp transition zone between the acidic and alkaline region in the brick. This zone resulted in a large electrical potential gradient due to the local depletion of ions. The experiments were conducted with constant voltage, and due to the large potential gradient in the transition zone, the electrical field diminished in the remaining brick. Consequently, the desalination stagnated and sufficient desalination could not be obtained. In addition to the pH changes also changes in the redox conditions at the two electrodes result from the electrode processes (1) and (2) so oxidizing conditions are prevalent at the anode and reducing conditions at the cathode. It is unlikely that the O\(_2\) and H\(_2\) will diffuse through the dense water saturated poultice. Another important electrode process occurs when Cl\(^-\) reaches the surface of the anode: \[ 2\text{Cl}^- + 2e^- \rightarrow \text{Cl}_2 \] The produced Cl\(_2\) can dissociate in water to form hypochlorite, which is an oxidizing agent.
However, again diffusion through the poultice into the tile is unlikely, and the redox condition in the tile expected unchanged during the desalination.

In previous research it has been shown calcite rich clay poultice can be used for neutralization of pH changes at the electrodes and two types have been tested: a calcareous clay for sampled at a brick work [8] and a pure mixture of kaolinite and calcite [15]. In these poultices the calcite buffers the pH changes and the clay gives workability, so the poultice can have optimal contact to the surface of the object to be desalinated. The two poultices were experimentally compared and both efficiently neutralized the acid from electrolysis at the anode neutralized the acid from electrolysis at the anode [13] and regardless poultice type, high initial concentrations of chloride (>0.34 wt%) was reduced to below (0.03 wt%). At the end of the desalination pH in the stones was similar to or higher than initially. Thus the acid from electrolysis at the anode was successfully neutralized by CaCO₃ in the poultices. When using the CaCO₃ rich poultices, the transition zone between low and high pH is moved from the stone to the anode poultice [16]. The increased concentration of OH⁻ ions in the material must be counterbalanced by cations (electro-neutrality) and in [17] it is suggested from numerical-chemical simulations that these are mainly Ca²⁺ from dissolution of calcium-carbonate in the anode poultice. There may thus be precipitation of Ca(OH)₂ in the material. Over time Ca(OH)₂ react with CO₂ from air and form CaCO₃, but neither Ca(OH)₂ nor CaCO₃ are considered damaging, because aqueous solutions of calcium hydroxide (limewater) have been used for many centuries to protect and
consolidate limestone [18]. In addition to neutralizing the acid, the poultice also gives good electrical contact between metallic electrode and stone, and it serves as sink for removed ions. When the clay poultices are removed after the desalination, the ions of the salts are removed with it.

In addition to the two electrode reactions (1) and (2) oxidation of Cl\(^-\) to Cl\(_2\) gas will also occur when chloride is transported to the surface of the metallic anode. As Cl\(_2\) is toxic, safety precautions must be taken if the electrochemical desalination is carried out indoors. There is also a theoretical possibility for reduction of NO\(_3^-\) at the cathode, but as electromigration transports the anions in the tile in the opposite direction this reduction is considered.

3. Materials and methods

3.1 Experimental tiles

Two XVIII century tiles from Palácio Centeno, Lisbon, Portugal were used (figure 2). The tiles were removed during renovation and loosened from the mortar on the back. They were part of tile panels, which suffered severely 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 (among others the experimental tiles) it was decided not to use them again. The original dimensions of the tiles were 14 x 14 x 1.5 cm, but the tiles had lost corners and had irregular shapes.
They suffered from severe loss of glazing. Initial samples were taken with hammer and chisel from the tiles for evaluation of the salt content: A (5 samples) and tile B (3 samples), see figure 2.

3.2 Experimental setup and procedure

The tiles had dried during indoor storage. They were too dry to be electrical conducting and thus they were wetted by spraying distilled water on the back side (opposite glaze) prior to the desalination experiments. The procedure was that little water was distributed over the back side of the biscuit, and the tile was left in a plastic bag for some days. This was repeated until the suction of water into the biscuit became slow. This procedure was chosen rather than soaking because soaking would mean wash off of efflorescence and surface near salts.

The tile was placed with the glazing down and two plastic frames with clay poultice were placed as shown at figure 1. The clay poultice was a mixture of kaolinite and CaCO₃ [15]. Electrode meshes were placed on the top of the poultice. The electrodes were inert meaning that they serve only as a source or sink for electrons without playing a chemical role in the electrode reactions. Finally the electrodes were connected to a power supply (Hewlett Packard E3612A). Tile A was placed in a desiccator over but not in contact with water during the desalination to have a high relative humidity around the tile to hinder drying. The desiccator though had a small opening in the top in order to let the
gases from electrolysis out. Tile B was instead wrapped in plastic film to hinder evaporation.

3.3 Desalination experiments

The power supply was set to supply a constant current, but the current was not kept at the same level all through the experiments. The applied current in the two experiments were: (Tile A) 10 mA in 14 days, 5 mA for 22 days, decreasing gradually from 5 mA to 2 mA during 25 days and (Tile B) 10 mA in 36 days, 5 mA in 23 days, decreasing gradually from 5 mA to 2 mA during 24 days. The reason for the changes in current was an increasing resistance during the experiments resulting in an increased voltage (Ohms 1st law) and when this maximum was reached the 10 mA could no longer be obtained and the current was manually decreased to 5 mA. Later when 5 mA could not be applied the current decreased gradually at a constant voltage of 136 V.

The poultice was changed every 7 days. At every change of poultice in the last period current increased 1-2 mA for a short period. The charge transfer per weight of tile was almost similar in the experiments, 140 and 150 C/g, respectively.

The overall experimental conditions are in table 1: dry weight of tile, initial water content, duration and charge transfer.
At the end of the experiments, the tiles were segmented with hammer and chisel (8 segments each). First the tile was segmented into two pieces running from anode to cathode. The pieces were separated into 4 segments each. The first segment 1(+) from each piece had been covered by anode poultice. Segments 2 and 3 had been without poultice cover. The fourth segment, 4(-), had been covered by cathode poultice.

3.4 Analytical

Each tile segment and clay poultice were weighed, dried at 105 ºC for 24 hours and weighed for calculation of water content (water/dry matter). The dry weight of the tiles (table 1) is the sum of dry weights of all segments. The dried segments were powdered in a mortar. Salts were extracted from the powder (or poultice) in distilled water (10 g in 25 ml). After 24 hours agitation, pH was measured with a pH electrode in the suspension, which was subsequently filtered and concentrations of Cl\(^{-}\), NO\(_3\)^{-} and SO\(_4^{2-}\) were measured by ion chromatography. The concentrations given in this paper are all based on dry matter.

SEM-EDX was used to investigate salt crystallization under the glaze before and after desalination. Small pieces of disintegrated glaze were removed from the tile and investigated with the glaze down.
4. Results and discussion

4.1 Salts in experimental tiles before desalination

The average initial concentrations and standard deviations of Cl⁻, NO₃⁻ and SO₄²⁻ of the tiles are shown in table 2. The concentrations are similar in the two tiles. There is neither a common European nor a Portuguese guideline on acceptable concentration levels for salt in building stone. To evaluate the salt concentrations the only accessible threshold values are from the Austrian ÖNORM B 3355-1 [19] and these threshold values are in table 2. The concentrations of Cl⁻ and especially NO₃⁻ are high compared to the threshold values. The SO₄²⁻ concentration on the other hand is below the lowest threshold value. The original position of the experimental tiles in Centeno Palace is unknown, but the high nitrate concentration suggests that animals have been kept near these tiles. Based on molar concentrations the relations between NO₃ and Cl are 1.7 and 1.5 in the tiles.

The glazing is generally lost from the outer edges of the tiles (figure 2), which is a common pattern for salt contaminated tiles [2]. The glazing of the experimental tiles is cracked and disintegrated in flakes few mm from the edge of the glaze. When removing such loosened flakes and investigating the surface opposite to the glazing in SEM, salt crystals are seen on every flake investigated (figure 3 is an example from a tile from Centeno Palace). Elemental mapping (SEM-EDX) reveals that these crystals are NaCl. Nitrogen is not found under the glaze even
though the overall concentration of nitrate in the tiles is very high (table 2). This shows that different salts behave differently as described in e.g. [20]. The salt crystals are probably worsening the disintegration of glaze, but whether the crystallization occurred after disintegration or before cannot be concluded from this investigation.

4.2 Changes in pH and water content

The profiles of water content (figure 4) and pH (figure 5) in the tiles at the end of the experiments are shown as average values for the two rows from the segmentation. The initial pH in tile (A) and (B) are 8.2 and 8.5, respectively. The pH in the tiles increased during the desalination experiments with up to 2 pH-units. The acid produced at the anode is thus successfully neutralized by the poultice. The final water content in tile A must is almost constant at about 13% throughout the tile, while the water content varies more in tile B (between 9.5 and 13%) (figure 4). The tiles had dried out from initially 17% and 13%, respectively. The electric resistance of a tile depends both on the water content and the ionic concentration in the pore solution and the mutual influence can to some extent be determined by measuring spontaneous potentials (streaming potentials) during rising damp [21], however such measurement was not included in the present investigation.

4.3 Chloride and nitrate concentrations in tile after desalination
Figure 6 shows final concentration profiles of Cl\(^-\) and NO\(_3^-\) in the tiles (average concentrations of the two profiles from the segmentation). There is a good agreement between the two profiles from each tile such as was reported in [5]. Thus possible concentration variations were leveled out during treatment. All concentrations of Cl\(^-\) and NO\(_3^-\) were well below the lower level of the ÖNORM [19], so the desalination was successful. The average molar concentrations for NO\(_3^-\) and Cl\(^-\) are similar. For chloride the concentrations were 3.3 m mole/kg and 2.8 m mole/kg for experiment A and B, respectively. For nitrate the corresponding concentrations were 3.2 m mole/kg and 3.5 m mole/kg.

Compared to previous experiments with electrochemical desalination of tiles from Centeno Palace [4, 5] the present results are much better in relation to NO\(_3^-\) removal. In the tiles from previous work, the initial NO\(_3^-\) concentration was lower (48-97 m mol/kg) than in the present investigation and the tiles were also less damaged (compare photos of tiles from [4] and figure 2). The charge transfer per dry mass of tile in the previous experiments was lower than in the present experiments. Insufficient NO\(_3^-\) removal was reached in the previous investigations, whereas NO\(_3^-\) removal progressed fine from the beginning of the experiments in the present investigation (figure 7). On the contrary to NO\(_3^-\), the Cl\(^-\) removal progressed well in previous and present experiments, with decreased concentrations all through the tiles, showing that the current had passed through the entire volume of the biscuit. Thus an inhomogeneous electric field distribution
is not the cause for the poor NO$_3^-$ removal in previous experiments. Neither is the reason a too low charge transfer, as it is seen from the new experiments (figure 7) that both NO$_3^-$ and Cl$^-$ were removed from the beginning of the experiments and at about the same rate. The conditions during the experiments from [4, 5] must have favoured NO$_3^-$ in non-ionic form, because otherwise NO$_3^-$ would have been transported towards the anode similar to Cl$^-$. The water content at the end of the experiments was few percentages higher in the tiles of the present investigation (in most segments 13%) than in the previous investigation (10.5-11%), and this lower water content may have been a limiting factor in [4].

Small pieces of disintegrated glaze were investigated by SEM-EDX after the desalination and in neither of the investigated pieces Cl, N or S were found. This shows that the desalination was also successful in relation to desalination of the interface between biscuit and glaze.

**4.4 Removal rates**

The accumulations of Cl$^-$ and NO$_3^-$ in the anode poultice based on the concentrations, which were measured every time the poultice was changed, are shown in figure 7. The desalination develops very similar in the two experiments. In the first period from starting the experiment until about 15000C, the Cl$^-$ removal is linearly related to the charge transfer ($R^2$ 0.992 and 0.997). The slopes for the Cl$^-$ removal curves were very similar in the two experiments (experiment A) $2.8 \cdot 10^6$ mole/C and (experiment B) $2.9 \cdot 10^6$ mole/C. After this first period,
the removal rate slows down and soon after the removal was insignificant. The
decrease in Cl\textsuperscript{−} removal rate is linked to the completion of the chloride removal, as it was seen from figure 6, that the final Cl\textsuperscript{−} concentrations in the tiles are very low. The pattern for NO\textsubscript{3}\textsuperscript{−} removal is similar, but the period with linearity is longer as the initial molar concentration of NO\textsubscript{3}\textsuperscript{−} is higher. The slopes for both the NO\textsubscript{3}\textsuperscript{−} accumulation curves are 3.3 \cdot 10^{-6} \text{ mole/C} (R^2 0.997 and 0.996). Also the NO\textsubscript{3}\textsuperscript{−} removal slows down after a period, where the removal is concluded.

The theoretical ionic mobility for NO\textsubscript{3}\textsuperscript{−} is 7.4 \cdot 10^{-8} \text{ m}^2/(\text{s V}) and for Cl\textsuperscript{−} 7.9 \cdot 10^{-8} \text{ m}^2/(\text{s V}), i.e. very similar. However, the removal rate for NO\textsubscript{3}\textsuperscript{−} is found slightly higher at figure 7. The relations between initial molar concentration of NO\textsubscript{3}\textsuperscript{−} and Cl\textsuperscript{−} are 1.7 and 1.5 in the two experiments. As the initial NO\textsubscript{3}\textsuperscript{−} concentrations are the highest, this influences the mutual relation between the removal rates so marginally more NO\textsubscript{3}\textsuperscript{−} is removed than Cl\textsuperscript{−} despite the similar ionic mobilities.

The transference number of an ion is the fraction of the total current carried by that ion. The transference numbers of Cl\textsuperscript{−} or NO\textsubscript{3}\textsuperscript{−} can be found as the moles in the poultice at the anode after a certain charge transfer divided with the total charge transfer (Q) found as: Q = I \cdot t/F, where I is the current, t the time in seconds and F faradays constant. The transference numbers calculated on basis of the mass transported into the anode poultice are for experiment A for NO\textsubscript{3}\textsuperscript{−} and Cl\textsuperscript{−} 0.32 and 0.27, respectively, and for experiment B 0.29 and 0.28. The sum of transference numbers for all ions (cations and anions) in a system is always 1.0. During the
first period, the sum of transference numbers for NO$_3^-$ and Cl$^-$ is about 0.6 based on this calculation. The calculated transference numbers must however be expected being too high, because the fraction removed by diffusion is included in the calculation. Pedersen et al. (2010) [11] compared diffusion and electromigration of SO$_4^{2-}$ into the same type of clay poultice. They found that at the part of the stone next to the clay poultice was initially desalinated well from diffusion, but not the central part of the stone, where significantly better desalination was obtained by electromigration. In [11] and [13] it is seen that electromigration results in profiles for anions with low concentration closest to the cathode poultice and high concentration closest to the anode poultice. When changing the anode poultice, there is a steep concentration gradient between poultice with neglectable concentration and the biscuit next to the poultice with high concentration, and this steep concentration gradient causes diffusion into the poultice. Hereby the calculated transference numbers are thus too high as they include diffusion, but never the less the transport numbers must be anticipated very high and almost all current in the first phase carried by target ions.

The removal into the poultice (figure 7) occurs at the same rate untill almost complete desalination. After Cl$^-$ was removed, the resistivity increased and the applied current was decreased from 10 mA to 5 mA. A similar increase in resistivity at the time for completing the NO$_3^-$ removal was not seen, but a more gradual resistivity increase after this phase was found. Had an increase in resistivity been found here as well, it would have been possible to use the
resistivity changes as an indication for the completion of the desalination process, which would have been very useful in actual desalination actions.

Initial conductivity of both tiles is about 18 mS/cm (table 2) and at the end of the experiments it is decreased to below 0.7-1.0 mS/cm. The difference in conductivity between the two tiles is small taking into account that experiment B continued 5 weeks after the removal of both anions compared to 2 weeks in experiment A. In the last period other ions than Cl\(^{-}\) and NO\(_3\)\(^{-}\) are major charge carriers. Among these OH\(^{-}\) as tile pH increases. Figure 8 shows accumulation of SO\(_4\) in anode poultices. The removal rate increases significantly after the removal of Cl\(^{-}\) and NO\(_3\)\(^{-}\). The removal rate is though still 30 times lower than for the two other ions in the initial phase, as the slope of the linear trend line for the last 6 points (experiment A) is \(1 \cdot 10^{-7}\) mole/C (R\(^2\) 0.98). Reasons for this slower removal rate are lower solubility of sulfate salts and lower ionic mobility (\(\frac{1}{2}\)SO\(_4\)\(^{2-}\) 4.2 \(\cdot\) 10\(^{-8}\) m\(^2\)/(V s)). Sodium sulfate as single salts causes damage at lower concentrations than sodium or potassium nitrate [22]. Thus removal of SO\(_4\)\(^{2-}\) may be important to stop the decay. However, in the present work the initial concentration (<0.05 wt%) was lower than the lower limit for damage from Na\(_2\)SO\(_4\) (0.25 wt% corresponding to 0.17 wt% SO\(_4\)\(^{2-}\)) found experimentally with limestone [22] and the lower limit of the ÖNORM [19].

5. Conclusions
Electrochemical desalination of highly salt damaged XVIII century tiles from Palácio Centeno, Lisbon, Portugal was successful. The concentrations of chloride and especially nitrate were very high initially (about 280 m mol/kg and 450 m mol/kg, respectively). After the treatment the concentrations decreased to less than 6 m mol/kg, which is considered a sufficiently low concentration for the salt decay to stop. Very important is the finding that no salt crystals were found under the glaze after treatment as was the case before.

The fraction of the applied current carried by chloride and nitrate during the desalination was very high meaning a high current efficiency. The poultices at the electrodes were changed every week, and diffusion from the high concentration in the tile next to the anode (continuously transported there by the applied electric field) into the poultice occurred, seen from the fact that more ions were removed than could be explained by the charge transfer. So both electromigration and diffusion were important transport mechanisms for the salt out of the tile.

Nitrate and chloride were removed at the same rate in the first phase of the experiments, but as the molar concentration of chloride was the lowest, the tile was depleted for chloride first. The initial sulfate concentration was low but when the more mobile chloride and nitrate were removed to a low level removal of sulfate started.

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References


<table>
<thead>
<tr>
<th>Exp.</th>
<th>Dry weight (g)</th>
<th>Initial water content (%)</th>
<th>Duration (d)</th>
<th>Charge transfer ($10^3$ C)</th>
<th>During experiment</th>
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<tr>
<td>A</td>
<td>218</td>
<td>17.2</td>
<td>61</td>
<td>32.1</td>
<td>In desiccator</td>
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<tr>
<td>B</td>
<td>358</td>
<td>13.0</td>
<td>83</td>
<td>53.8</td>
<td>In plastic</td>
</tr>
</tbody>
</table>

Table 1: Experimental conditions for the two electrochemical desalination experiments. Initial weight is for the tile segment after taking samples for initial content.
<table>
<thead>
<tr>
<th></th>
<th>Tile A</th>
<th>Tile B</th>
<th>Threshold value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(No risk/critical limit)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(^-) conc. (m mol/kg)</td>
<td>276 ± 15</td>
<td>277 ± 23</td>
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<tr>
<td>NO(_3^-) conc. (m mol/kg %)</td>
<td>485 ± 58</td>
<td>413 ± 33</td>
<td>8.1/24</td>
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<tr>
<td>SO(_4^{2-}) conc. (m mol/kg)</td>
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<td>8.5 ± 0.1</td>
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<tr>
<td>Conductivity (mS/cm)</td>
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<td>18.8 ± 0.8</td>
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<td>Water content (%)</td>
<td>3.2 ± 0.2</td>
<td>3.0 ± 0.3</td>
<td></td>
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</table>

Table 2: Initial concentrations of Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\) in tiles and threshold values from the ÖNORM [19] (below lowest value no risk, above the highest value damage must be expected, and in between evaluation must be carried out in each specific case). Initial pH, conductivity and water content before wetting the tiles are given.
Figure captions

Figure 1. Laboratory setup and principle in electrochemical desalination of single tile. The electrodes are placed in clay poultice on the surface of the biscuit opposite to the glace

Figure 2: The two salt damaged tiles used in the experimental work.

Figure 3: Example of SEM-EDX investigation of the back side of lifted glaze. The elemental mapping reveals that the salt crystals are NaCl

Figure 4: Water content in tiles at the end of desalination experiments.

Figure 5: pH in tiles at the end of desalination experiments.

Figure 6: final concentration profiles of Cl and NO3 in the tiles

Figure 7: Accumulations of Cl and NO3 in the anode poultice

Figure 8: accumulation of SO4 in anode poultice
Figure 1.

Anode processes:
\[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) + 2e^- \]
\[ 2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \]

Cathode process:
\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(\text{g}) \]

Clay poultece
Biscuit
Glazing
Na^+ → Cl^−
Figure 2
Figure 4

![Graph showing water content comparison between Tile A and Tile B.](image-url)
Figure 5
Figure 6
Figure 8

![Graph showing removal of SO4 vs charge transfer for Experiment A and Experiment B.](image)

- **Removed SO4 (m mole)**
- **Charge transfer (C)**

- **Experiment A**
- **Experiment B**