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ELECTRO-DESALINATION OF GLAZED TILE PANELS – DISCUSSION OF POSSIBILITIES

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Abstract

Glaze is lost from tiles in tile panels due to presence of soluble salts and this means loss of important heritage. The present paper discusses the possibility to apply electro-desalination. An in-situ test has not been performed yet, but encouraging results have been obtained with different parts of the system. Single tiles, a variety of porous stones and the mortar on the back of a tile have all been electro-desalinated successfully in laboratory scale. Thus individually, all parts of the wall with tile panel can be electro-desalinated. The interface between mortar and tile can be problematic. In the few experiments conducted on tiles with attached mortar, the mortar was desalinated to a higher degree than the biscuit and successful desalination of the biscuit through the mortar requires further research.

In-situ pilot scale tests were performed on highly salt-contaminated walls without tiles by placing electrodes at the same side of the wall. Thus it may be possible to desalinate tile panels, without any physical damage of the fragile glaze, by placing electrodes on the back of the wall or by removing some tiles, placing electrodes in their spaces, and extracting the salts from there before the tiles are placed back again.

1. Introduction

Ceramic tiles, azulejos, are an important Portuguese cultural heritage. They have been used continuously during five centuries. Regrettably many tiles are lost due to decay. 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 bevelled and, when mounted together to form a panel, their edges contact [1]. This may constitute a problem in cases the tiles are wet for a long period causing swelling and subsequent crack and damaged glazing. Today many degraded tile facades are in urgent need of maintenance [2]. Soluble salts are a major cause of decay, and aside from human actions, are likely the most important cause of decay and loss of single tiles as well as whole panels [1]. The damage caused by soluble salts is generally due to their accumulation and phase transition at or near the surface of the object, or between layers, as a result of moisture transfer processes [3]. 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 [4]. Tiles are applied after being soaked so that they are dilated, in order that further (thermal or hydric) expansion does not cause cracking. But afterwards, they contract. Therefore, the joints may be slightly open when rain hits the panel. This will influence the distribution of salts in the wall. Mimoso et al [1] 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 dry walls. Tiles with manufacturing defects (glaze partially cracked or delaminated) thus offer easy routes for moisture propagation and salt crystallization.

In-situ treatment options for removal of salts are few. Poultice technique (a poultice is applied to the surface and salts are transported out from the tile by diffusion and/or advection) suffers from the need for the poultice to be applied to the often fragile glazed surface, thus physical damage may be hard to avoid. Also, in areas where glaze is intact transfer is nil.

The present paper deals with development of electro-desalination for in-situ treatment of tile panels. A discussion of possibilities and limitations of the method for desalination of tile panels is given on basis of already published work with results ranging from desalination of single tiles to wall sections (without tiles).

Tiles are placed on the wall on a bed of mortar (figure 1). It is important to remove salts from all parts during the in-situ electro-desalination, otherwise the tiles will soon be salt infected again from salts entering from mortar and wall. In this paper electro-desalination of the different parts: wall, tile bed, ceramic biscuit and glaze are first discussed separately. Influence from interfaces between the different materials/parts is then discussed and finally the possibility for in-situ electro-desalination of tile panels is evaluated, focusing on the possibility to place the electrodes around the panel to avoid any further damage.

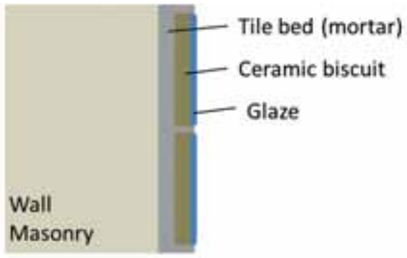

Figure 1: Cross section of tile panel. This paper discusses electro-desalination of the four single parts followed by a discussion of in-situ treatment of tile panel and support

2. Principles of electro-desalination

The main transport mechanism for salt ions in a moist, porous material under application of an electrical potential gradient is electromigration, which electro-desalination is based on. During the process, the concentration of dissolved salts will decrease in the porous material as the

dissolved ions concentrate around the electrode of opposite polarity. The overall principle of electro-desalination is shown in figure 2. The electrode compartments consist of an inert electrode placed in a clay poultice. The electrode compartments are placed on the surface of the porous material to be desalinated. The optimal placement is determined by several factors, which are discussed later in this paper.
The dominating electrode processes are electrolysis of water: $H_2O \rightarrow 2H^+ + ½ O_2$ (g) + $2e^-$ (at the anode) and $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (g) at the cathode. When the removed chloride ions reach the anode they can be oxidized to Cl_2 from the electrode process: $2Cl^- \rightarrow Cl_2$ (g) + $2e^-$. Electrolysis influences the pH around the electrodes. It is necessary to neutralize acidification at the anode in order to prevent decay of the material to be desalinated. Hendrix et al [5] underlined how important it is to avoid acidification, as in experiments without pH neutralization the stones were severely damaged close to the anode. This was confirmed by [6] who reported that buffering of the acid produced at the anode was important to avoid decomposition of the stone (seen as increased porosity due to dissolution of calcite) in case no buffering system was used. In addition, they reported gypsum formations in the region closest to the anode both with and without poultice, but a higher degree of gypsum was seen in the setup without poultice. Also in order to obtain sufficient desalination pH neutralization can be crucial. Kamran et al. [7] 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. This zone resulted in a large electrical potential gradient due to a local depletion of ions here. So for different reasons, the metallic electrodes should not be placed directly on the material to be desalinated.

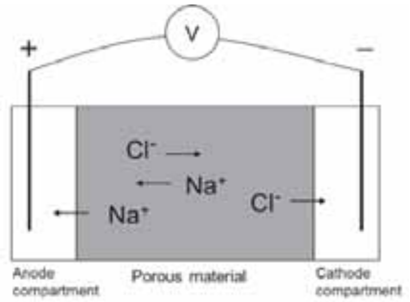

Figure 2: Principle of electro-desalination

Carbonate rich clay poultice can be placed between the electrodes and the stone for neutralization of pH changes. Calcareous clay for brick production or a mixture of kaolinite and calcite both efficiently neutralized the acid [8]. The acid was neutralized by the $CaCO_3$ in the poultices. In the cathode poultice and in the porous material there may be precipitation of $Ca(OH)_2$ in the material as a result of the alkalinisation from the cathode [9]. Over time $Ca(OH)_2$ reacts with CO_2 from the air and forms $CaCO_3$. Neither $Ca(OH)_2$ nor $CaCO_3$ are considered damaging, because aqueous solutions of calcium hydroxide (limewater) have been used for many centuries to protect and consolidate limestone. 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.

3. Electro-desalination of the different parts in a tile panel

In this chapter the experimental results with the different parts of the tile panel shown in figure 1 are discussed separately.

3.1 Single tiles – biscuit and glaze

Experiments have been reported with electro-desalination of single tiles in the laboratory [10-12]. The experimental setup of these is illustrated in figure 3a. The tiles were placed with the glaze down and because they had dried out during indoor storage, water was sprayed on the back side before placing the electrode compartments (poultice and inert electrode mesh) as far apart as possible. The tile and electrode compartments were wrapped in plastic to hinder evaporation of water, which would hamper the passage of electric current. A constant current was then applied to the electrodes. Moist pores are needed in order to be able to have passage of current through the biscuit. In cases, where salt decay is problematic, waster must be present at least during some periods and it is assumed that it is not neither necessary to add extra water or cover the wall as in the laboratory atmosphere with very low RH.

The first results reported on electro-desalination of single tiles were obtained with XIX century tile segments spiked with NaCl [10]. Removal efficiencies of 96% Cl was reached in less than 6 days. Following this good result, experiments with spiked tiles, experiments were conducted with 18th 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. The charge transfer in the electro-desalination experiments was too low in the experiments to obtain full desalination, but promising results were obtained as significant decreases (>81% Cl^-, ~ 59% $NO3^-$ and ~ 22% SO_4^{2-}) were seen. In Ottosen et al [12] the duration of the experiments was long enough to obtain sufficient desalination (2-3 month). There is neither a common European nor a Portuguese guideline on acceptable levels for salt in building stone. To evaluate the salt concentrations, the only accessible threshold values are from the Austrian ÖNORM B 3355-1 [13] and these are chosen as a first approach here, though these limiting values are much debated. In relation to the ÖNORM the concentrations of Cl^- (9900 mg/kg) and especially NO_3^- (30,600 mg/kg) were very high in the tiles (exceeding the concentrations where desalination is advised). After the electro-desalination the concentrations of both Cl^- and NO_3^- were well below the lower level of the ÖNORM (which are respectively 300 mg Cl/kg and 500 mg NO_3^-/kg), so the desalination of the biscuit was successful.

Figure 3: (a) Experimental setup for desalination of single tile; (b) 20th century tile used in lab experiment.

Large parts of the glaze and parts of the biscuit were lost in the Palácio Centeno tiles, presumably due to salt decay. The most severe damage was seen from the outer edges towards the centre of the tile [1]. Salt crystals (NaCl) were clearly identified under the lifted glaze by SEM-EDX, butafter electro-desalination no crystals were found under the glaze. Thus this important interface was successfully desalinated [12]. Salt crystals cannot directly be reached by the electric field as they carry no electric charge. During electro-desalination salt crystals must have been dissolved into ions in the pore solution, likely by the penetration of water from the wet poultice, hereby mobilizing them for electromigration. When free ions are removed, equilibrium will change towards dissolution of more crystallized salts and the new ions can subsequently be removed by electromigration, so a low and harmless concentration of salt was obtained over time. It must be investigated, if the water in salt damaged tile panels is sufficient for such dissolution of salt crystals over time.

The fraction of the applied current carried by Cl^- and NO_3^- during the desalination was very high meaning a high current efficiency. During the desalination Cl^- and NO_3^- were removed at the same rate. The initial sulphate concentration was low, but when the more mobile chloride and nitrate were removed to a low level removal of sulphate started [12].

An experiment with electro-desalination of a Portuguese 20th-century tile (figure 3b) has also been conducted (not previously published). The average initial concentrations were 700 mg Cl^-/kg and 930 mg SO_4^{2-}/kg and thus the salt contamination was much less that the older tiles from Palacio Centeno. After 3 weeks with 1 mA applied 76% Cl^- and 87% SO_4^{2-} were removed. Hereby it was shown that also this biscuit type can be desalinated.

3.2 Tile bed and interface between tile bed and tile

Lime mortars have been used since ancient times in masonry, renders, plasters, and also as adhesive agents for tiles, namely between 16th and mid. 20th centuries. This type of mortar is known to be compatible with old masonry and ancient ceramic tiles [14].

Brammer & Sveegaard [15] and Ferreira et al [16] reported laboratory results with electro-desalination of three tiles from different centuries. Mortar was attached to the tiles in these investigations (see figure 4). Each of the three tiles was broken. The tiles were: 17th -century tile from the Alentejo Region (mortar very hard and unfortunately not considered original), 18th-century tile from Palacio Centeno, Lisbon (mortar very porous and loose, considered original) and 20th-century tile of unknown origin (mortar was hard, but is considered original). Initial samples were taken from both tile and mortar prior to the desalination experiments. From the first two tiles it was only one sample from both. The 20th -century tile was separated into two pieces where one was used to find the initial salt concentration and the other for the desalination experiment.

As in the experiments with single tiles, the tiles were placed with the glaze down. Water was sprayed on the mortar, which was now the upper part and the electrode compartments were placed on the mortar surface. The overall conclusions from the electro-desalination experiments with tile and mortar attached were:

17th century tile: The glazing of the tile did not show sign of salt decay and the concentrations in the initial samples were also very low 93 mg Cl/kg and 130 mg NO_3/kg in the mortar and 53 mg Cl/kg and 42 mg NO_3/kg in the biscuit. Still it was decided to see if the salt content could be lowered by electro-desalination, which was the case. The removal after 7 days with about 1 mA applied were in average 51% Cl and 83% NO_3/kg in the mortar and 15% Cl and 64% NO_3 in the biscuit. Thus even at such low concentrations salt was removed in the applied electric field. The highest decrease was obtained in the mortar, but the concentration was also decreased in the biscuit [15].

18th century tile: Very high initial concentrations in both mortar (6600 mg Cl^-/kg and 14,000 mg NO_3^-/kg) and biscuit (6600 mg Cl^-/kg and 14,000 mg NO_3^-/kg) were found. During the 24 days of experiment the current was gradually increased from 5 to 10 to 20 mA as the voltage (reflecting the overall resistivity) was very low. From the mortar was removed 91% Cl^- and 84% NO_3^- and from the biscuit 42% Cl^- and 9% NO_3^- [15-16]. The desalination was not completed in this experiment as too high concentrations remained, however, as the voltage was still low at the end of the experiment and as the concentrations of salt ions continuously increased in the poultice the desalination could have progressed longer [17]. The percentages of salt removal from the mortar were significantly higher than from the biscuit in this experiment.

20th century tile: Compared to the Önorm neither of Cl^-, NO_3^- and SO_4^{2-} exceeded the limiting value were salt removal is advised. However, the average SO_4^{2-} concentrations were high both in mortar and biscuit and the concentration varied considerably, so it was decided to perform electro-desalination even if the adapted upper limiting values from the ÖNORM were not exceeded (the concentration level falls within the category where individual evaluation is advised). This because some sulphate salts are known to be highly damaging. In the reference piece the average concentrations with standard deviation were: mortar 1540 ± 1490 mg SO_4^{2-}/kg and biscuit 650 ± 590 mg SO_4^{2-}/kg. After electro-desalination the concentrations were: mortar 150 ± 83 mg SO_4^{2-}/kg and biscuit 120 ± 32 mg SO_4^{2-}/kg. This corresponds to a removal on average of 90% from the mortar and 82% from the biscuit.

Figure 4: experimental tiles with mortar. Top: 17th century tile from Alentejo (PT); middle: 18th century tile from Palacio Centeno, Lisbon; bottom: 20th century tile of unknown origin.

The interface between mortar and tile can be problematic for in-situ electro-desalination in cases where the tile is partly loosened and there is air-filled space between them. Then passage of current is not possible in this zone. In all three tiles the salt ions were removed better from the mortar than tile, but this may reflect that the electrodes were placed on the mortar and not the biscuit. Salt ions were removed over the interface in all cases. The adhesion mechanism between tile and mortar is ruled partially by physical forces, such as Van der Walls and the suction of fresh binder by the tile, and partially by chemical links. Thus, the chemical and mineralogical composition of the bonding agent, i.e. the mortar, may be critical for an appropriate bond [14]. The interface can be very weak and experiences focusing on mapping interface properties, where the interface is limiting the electro-desalination process of the tile through the mortar must be obtained from experimental work, followed by finding a method where these situations can be found while the ties are still in place.

3.3 Brick and natural stone

Electrochemical desalination of different porous matrices has been tested in the laboratory, namely **baked clay bricks (**Handcrafted red bricks for renovation purposes [18-19], yellow brick [20], and red bricks [21]) and **natural stones (**posta and cotta sandstones [22], Gotlandic Sandstone [6]), Nexø sandstone [23], and granite [24]). Electro-desalination was successful in every case, and thus the success for desalination of a tile panel is not considered to be dependent on the porous material of the wall itself. The influence on electro-desalination of the interface between wall and mortar must be investigated similarly to the interface between tile and mortar. However, no such experiments have been conducted yet.

4. Pilot tests with masonry without tile

Ottosen and Hansen [25] summarize results from four small (2-6 electrode units) and one larger (74 electrode units) in-situ pilot scale tests for electro-desalination of masonry (natural stone and brick masonry). In every case, the electrodes were placed at the same side of the wall and with alternating polarity. When the electrodes are placed like this, the electric field is strongest close to the surface, but will distribute into the wall as shown schematically in figure 5a. When the electrodes are at the same side, the salt concentration decreases closest to the electrodes first and over time the desalination progresses into the depth of the material [18]. Figure 5b is an example of a pilot scale plant for electrodesalination. Neither of the pilot scale tests can be regarded as the final proof of concept, as full desalination has not been obtained yet. Every test was unfortunately stopped before full desalination due to limited project-duration. However, when they were stopped, the transference number for the target ion was still high, and desalination could have progressed further if the experiment had been prolonged. The large pilot scale plant covered about 25 m^2 surface of a limestone wall of a historic warehouse. The wall was highly contaminated with NaCl (7300 mg Cl/kg). A total of 3.8 kg chloride (6.3 kg NaCl) was removed during 390 days [8]. A small pilot scale experiment was close to full desalination. The main pollutant was NaCl (initial levels: 1400 -4000 mg Cl/kg. The Cl^- concentration in the masonry below the cathode and between the electrodes was decreased to a sufficient level in 10 cm depth. The concentration below the anode was decreased to a level of 1800 mg Cl/kg, which was still too high compared to the ÖNORM (300 mg/kg).

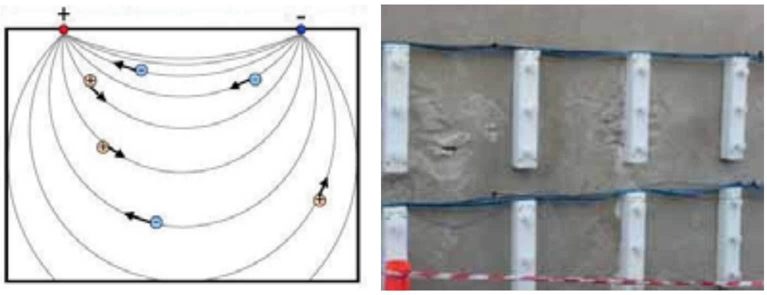

Figure 5: (a) principle of electro-desalination of wall with electrodes placed at the same side of the wall and distribution of electric field lines in case of a homogeneous material. (b) Photo from a pilot scale plant for electro-desalination of walls.

5. Discussion on possible in-situ desalination of tile panels

For in-situ electro-desalination of tile panels the electrodes should not be placed on the surface with the fragile glaze. As the overall transport mechanism for the salt removal is electromigration advantage can be taken of the electric field lines to distribute over a certain volume. The electric field will be strongest where the conductivity is highest, and this must be expected to be close to the surface where the salt damage also develops. In laboratory experiments using bricks [18] it was clearly shown that the part of the brick closest to the electrodes was desalinated before the middle part, which was again desalinated before the lowest part of the stone. In sandstones cut in irregular shapes, parts of the stone not directly between the electric field were also desalinated, though later than the part between the electrodes [26]. These two studies show that electrodes do not necessarily need to be on each side of the object to be desalinated. This can be utilized when desalinating tile panels. In case there are no air cavities between wall-mortar-tile, it is likely that the desalination can be achieved by electrodes placed on the surface of the wall opposite to the tiles. Another option is to remove already loose tiles and place electrodes on the mortar where they were removed. The removed tiles should be desalinated ex-situ (e.g. by submersion) before placed in the tile panel again after electro-desalination.

There are several open questions, which need to be researched and answered. For example, the walls can be more than 1 m thick. This may limit the option of placing the electrodes at each side as the electrical resistance may be very high, and also the wall may not be in hydraulic contact all through. An option may here be to place the electrodes at the same side and focus on desalinating the wall closest to the tiles only.

The solubility of the salts is a determining factor for electro-desalination. All damaging salts are soluble as it is the cycles between solubilized and nucleated which causes the decay. However, if solubility is very low, electro-desalination will be very slow (years). We may need to wet the wall in periods with low RH or, alternatively cover the wall during treatment to keep the moist and hinder evaporation. In the pilot scale plants performed so far on walls without tiles, wetting was not necessary. When the supply of moisture and salts remains active after electro-desalination, as in the case of rising damp, salt induced decay will reappear over. A suggestion might be to estimate the rate at which the salts are supplied into the masonry again and plan for a new desalination action before a damaging level reappears.

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The various topics of the proceedings are within reinforcement corrosion (Corrosion mechanisms and propagation, modelling of service life, and corrosion prevention), electrochemical assessment methods (in both construction and geotechnical materials), electrochemical repair techniques (stopping corrosion, crack closure and desalination for heritage conservation) and electrochemical upgrading of waste for use in construction materials (concrete or ceramics).

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