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Final Thesis

**Development of
electrochemical
methods for
desalination of
porous materials**

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AIM

Natural stones have always been used as construction material for both decorations and structures, starting from the earliest times up to the present time. The decay of stone artifacts has always been a major threat to cultural heritage preservation and the difficulty in treating and consolidating these artifacts has led multiple studies into researching new methodologies and products for their conservation. Porous materials in particular are subjected to physical decay phenomena due to the presence of soluble salts absorbed from the surrounding environment.

This thesis focuses on studying an innovative technique that could be applied for salt extraction without damaging the material or utilizing harmful products. In the specific, this study concerns the development of a double electrode system in presence of poultices layers and of an electric current to gain a high cleaning efficiency. The purpose of developing an electrode based electrochemical system is to create a possible alternative to traditional cleaning methods that are not always efficacious.

1. INTRODUCTION

The degradation of porous building materials is conditioned by the composition and porosity of the material, its production history, and environmental conditions [5].

These factors can often occur simultaneously, thus making the identification of the degradation forms quite difficult and requiring interdisciplinary studies [16].

In the next chapter, a short description of the physical decay in porous materials will be presented, with a particular focus on the degradation processes due to the presence of soluble salts. After, a summary of the traditional and innovative methods applied to extract soluble salts from porous stone.

1.1. POROUS MATERIALS AND PHYSICAL DECAY

Rocks are not whole in their mass, cracks and pores are frequently found in most materials, originated from the solidification process of the rock and external stresses [1, 17]. They make the sample brittle and stiffer, due to the inner continuous network and make the material permeable to fluids [3].

Water and external harmful elements absorption into a porous material depends on the porosity of the material itself. The shape and size of the porous system influences in turn the greater or lesser harmful effect that can be generated by alteration agents or by the water, such as those caused by the freeze-thaw events or by soluble salt crystallization. Moreover, it is necessary to highlight that the pores (both the open and the closed) also influence the mechanical properties of the materials. A high porosity value, in fact, reduces the resistance against mechanical stresses, such as tensile stresses caused by static loads, thermal expansion, corrosion of metal entails, traffic vibration and so on [8].

Materials such as stones, concretes, and mortars which are often employed as construction building materials have a critical weakness in porosity and hydrophilic behavior. Moisture may be caused by the presence of water of external origin derived from the subsoil and attracted by the walls by the effect of capillarity. [2].

Most building materials are rich in groups of atoms like -OH, the presence of which make them wettable [16].

When a water drop touches a solid surface, adhesion forces internal cohesion stretches the liquid and form a curved surface (fig.1).

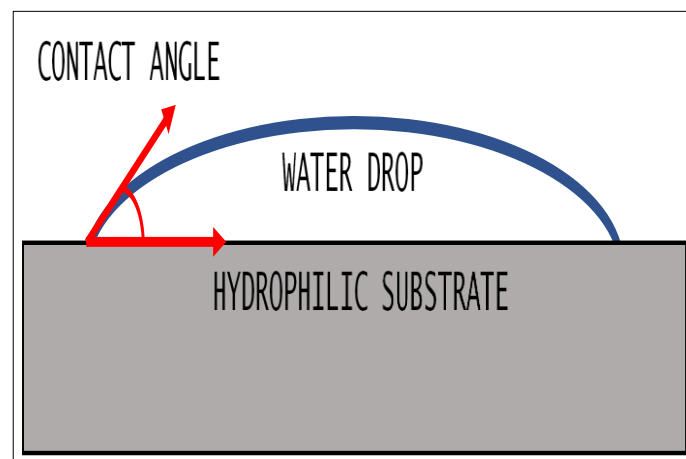


Figure 1 Curved surface of a water drop on a hydrophilic substrate [16].

When a liquid happens to be close to the surface of a container or another object (pores) the curve in the upper surface is called meniscus and it's caused by adhesion forces.

Water “climb” upwards in the materials and this motion is known as capillarity. It depends on the attraction between water molecules and the molecules along the pores (adhesion), as well as on interactions between water molecules (cohesion). Water rise inside a hydrophilic tube is greater as the pore gets thinner. The curved surface formed by water in the pores is called meniscus. It can be concave or convex, depending on the liquid and on chemical characteristics of the material in which water

is damping. In hydrophobic tubes the meniscus is inverted, water molecules are not attracted, and the liquid does not rise (fig.2).

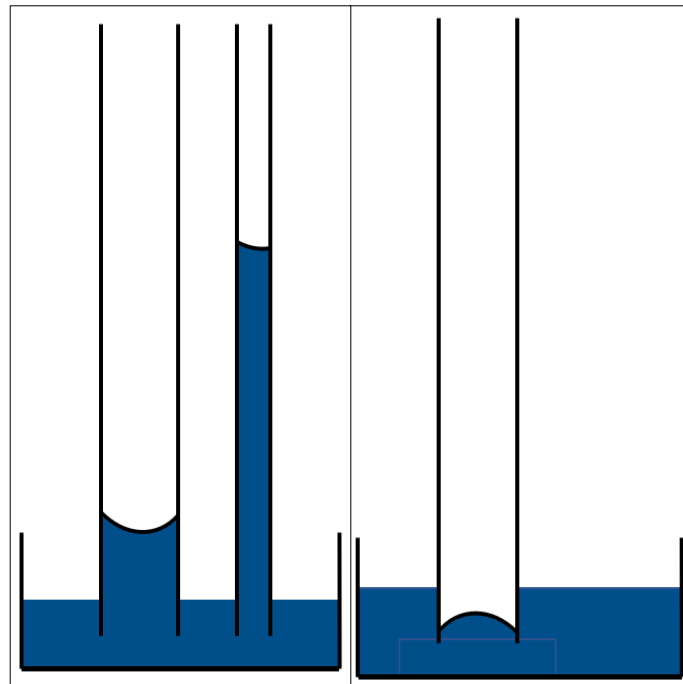


Figure 2 Capillarity behavior of different fluids [16].

When the porous materials get in contact with water, different decay processes may occur. Ice formation inside a wet porous material can cause damages whose entity obviously depend on the mechanical properties of the material itself, but most importantly on the pore distribution [16]. Damages will occur when the internal stresses due to ice formation becomes larger than the strength of the material. The sensibility of the material to frost damage is determined by the structure of the porous body and the size, shape and connection of pores which also influences the water distribution inside the material and the characteristics of the pore space to potentially form ice crystals [6].

Water crystallizes when temperature drops lower than 0°C , and in porous rocks it may occur also as a consequence of super-cooling or a decrease of the freezing point of the fluid. Supercooling

occurs when the temperature of a liquid or a gas is lowered below its freezing point without it becoming solid. It occurs when there is a lack of seed crystal or nucleus around which a crystal structure can form but, as in natural porous materials enough crystal surfaces are available, heterogeneous nucleation mostly occurs. The freeze point reduction instead concerns a variation of equilibrium conditions of the fluid, and, again, it is related to the pore space distribution. The smaller the pore, the stronger the water is strained, and therefore freezing at increasingly lower temperatures results. It has been observed that during cooling of natural building materials, due to their wide range of pore sizes, a heterogeneous crystallization occurs but, while water is already crystallized in larger pores, it can still be found in a liquid state when in smaller ones [15]. Ice crystals start to grow using the water available around them in larger pores but as they consume all the water available, they start to use the water from the capillary pores (fig.3) [16].

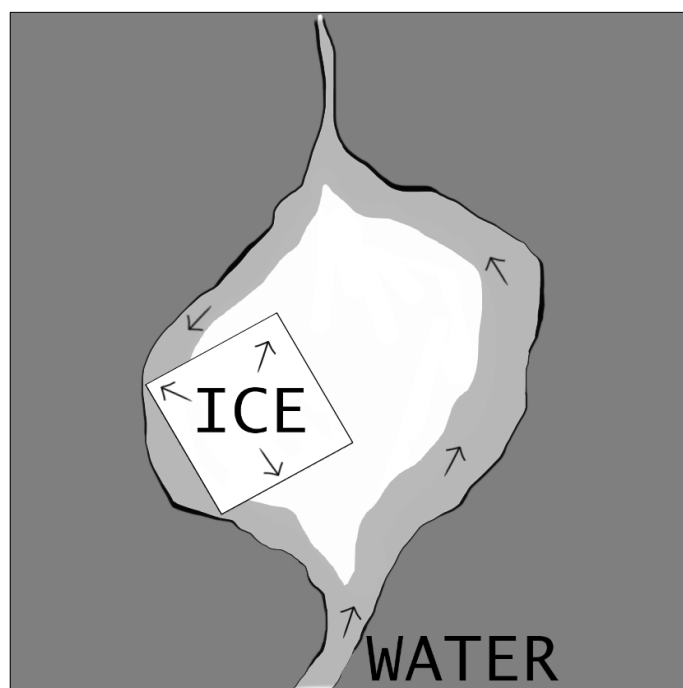


Figure 3 Growth of ice crystals in a porous system [16].

If large pores are quite numerous, the stone does not suffer stress, the growth of crystals stops before filling the pore space. Instead, when pores are small and numerous in respect to bigger ones, ice crystals can grow up to fill all the available space and create pressure on the pore's walls. The physical processes that can cause high pressures inside a porous material are the freezing of water as it determines an expansion of 9% resulting in a water pressure rise inside the cavity and, when cavities are almost ice filled, a flow of water can occur during the later stages of freezing. In this case the pressure rise is due to the flux of water into the cavities, which then freezes and increases the overall ice mass [18].

The presence of soluble salts is generally considered to be the most important physical deterioration cause for porous materials [10]. The presence of Salt in stone materials is the result of a combination of multiple phenomena and is like to be found not only in nearby-sea countries but even in far regions due to strong wind action. Marine aerosol is one of the major carriers of salts in buildings/artifacts. Because of certain meteorologic physical phenomenon, like rain, snow and hail or wind, the marine aerosol is originated from the rupture of the superficial film of seawater, producing small droplets called spray which will deposit on the surface of the material. Of course, after the evaporation of water, both soluble and insoluble particles that have originated from seawater remain, such as metals, organic substances and most importantly salts (NaCl mostly) [5].

Table 1 Salt components concentrations in Atlantic Ocean/Mediterranean Sea [5].

Salt	Atlantic O. g/L	Mediterranean S. g/L
NaCl	28.14	30.76
KCl	0.69	0.66
MgCl ₂	3.44	3.74
CaSO ₄	1.42	1.64
MgSO ₄	2.28	2.39

The previous tab.1 provides the concentration of salts in the Mediterranean Sea and in the Atlantic Ocean measured in grams/Liter. These are the leading source of soluble salts that may affect the durability of the stone artifacts [10]. The seaware can be also absorbed by the materials by direct contact, as in the case of flood or “high tide” that characterize the city of Venice and other cities in coastal zones. Other carriers of salts are related to the indirect action of soil salinization, a major process of land degradation affecting soil fertility and food production. The accumulation of soluble salts in soil happens as a consequence of evaporation process exceeding the precipitation one, therefore, salts are not leached but remain in the upper soil layers. Soil salinization can be both natural or artificial: Natural soil “primary” salinization occurs in arid and semi-arid climatic zones while the “Secondary salinization” is the term used to describe soil salinized as a consequence of direct human activities ° like the use of fertilizers that are enriched with soluble salts or calcium chloride commonly used to prevent freezing on the roads during the winter [11].

Soluble salts tend to crystallize within the pores of the material, especially in those that are close to the surfaces where the water evaporation easier occurs.

A porous stone material if saturated with soluble salt, will be damaged in a similar way to that resulting from freezing and thawing phenomena. Salt crystals will grow within the pores and through continuous repetition of wetting and drying cycles may produce an expansive force that will weaken the structure of the material [11,8,16].

As said in paragraph 1.1, the growth of crystals may happen inside the large and medium pores (larger than 10 micron) [2] while the capillary ones store the liquid and feed it to the growing crystals [16].

Because of this, materials with a large proportion of large pores than capillaries are less likely to undergo damage. The salt does not crystallize immediately upon reaching the saturation concentration during water evaporation, this happens because the ions attracted to the polar surfaces of the hydrophilic material resist the input to form a crystal nucleus. Depending mainly on the environmental conditions around the materials, crystallization may take place both on the surface and inside the material.

Low/moderate temperature and a medium/high relative humidity combined with low air velocity forms the optimal conditions that will generate efflorescences (fig.4) through a slow evaporation from a damp porous structure. Instead, warm, windy, and dry climate will favor sub-efflorescences. Very porous stones like tuffs or calcarenites may undergo alveolization (deep holes on the surface) due to sub efflorescence if located in warm, dry climates near the sea (fig.5).



Figure 4 Salt crystals growth on brick surfaces [17].

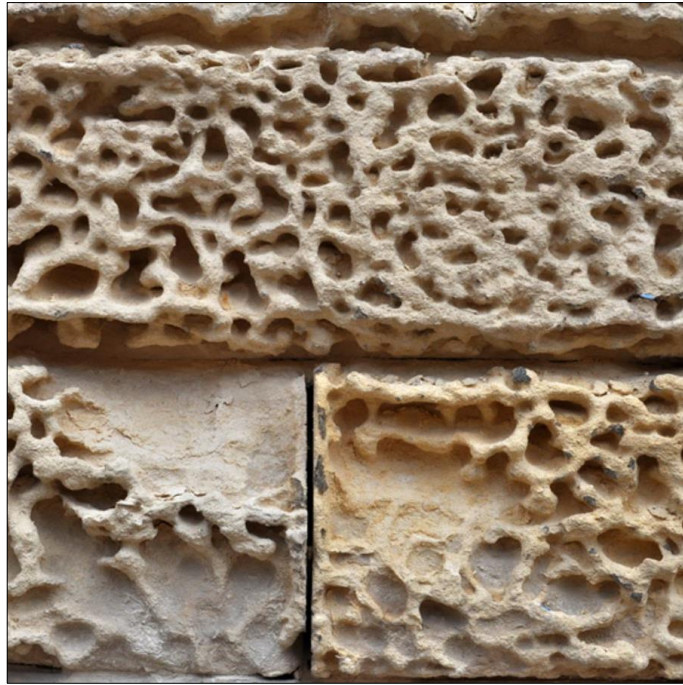


Figure 5 Alveolization on carbonate stone [4].

In porous sedimentary stones, saltwater travels mostly through the layers richer in capillary pores, and when these happen to be at the surface, crystallization occurs. Through the wind action, which accelerates the evaporation of salt enriched water, sub-efflorescences start to be produced. This will result in the formation of small cavities on the surface of the stone material, which will further damaged by the action of local whirlwinds whose gusts, which often carry debris, hit the surface with force (fig.6).

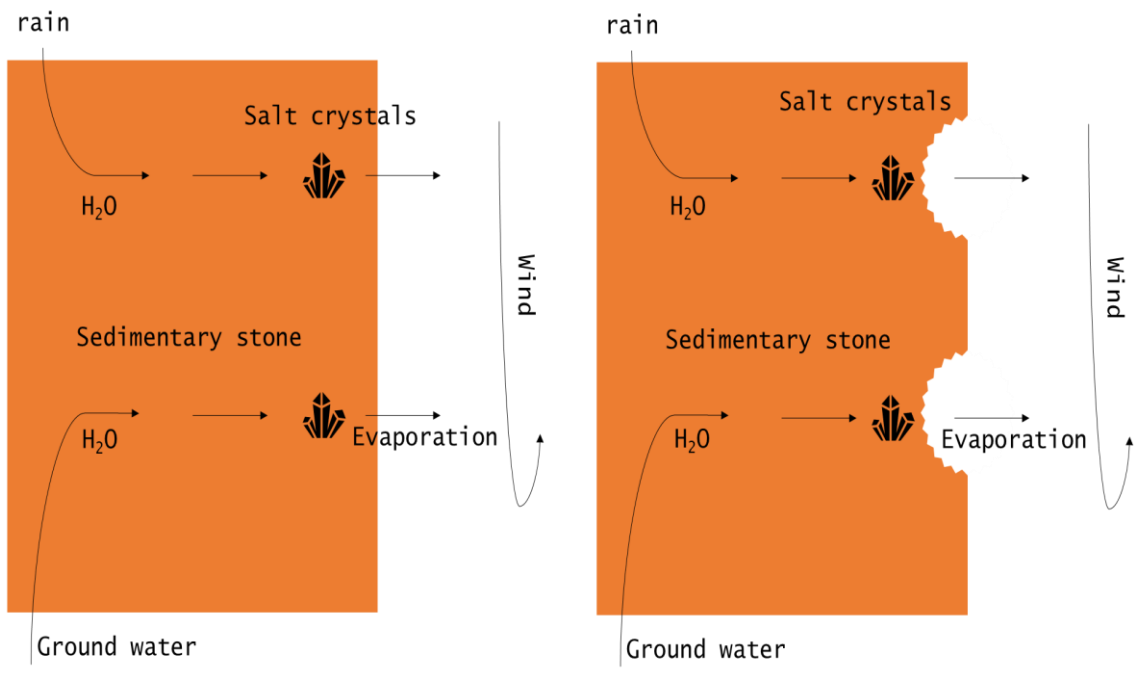


Figure 6 Wind erosion on salted carbonate supports [16].

Some salts may also change their hydration states in relation to the microclimatic conditions. Every change in hydration state produces a corresponding molar volume change, severely disrupting the internal structure of the stone. The rate of hydration may also be an important factor in the physical decay of the stone due to the presence of hydrate salts [3].

1.2. DESALINATION TECHNIQUES

Generally speaking, cleaning of the materials in cultural heritage aims to remove all dangerous substances like soluble salts, dust, compounds deriving from chemical degradation, pollutants and all the materials potentially dangerous for the conservation of the artifacts.

The choice of method must be able to selectively remove only the substances related to decay processes without damaging the material itself [16].

When high-porosity materials are affected by soluble salts, special clays with high absorption capacity (sepiolite or attapulgite) or cellulose are used as poultice in order to make more effective the salts extraction. Clay poultices are also useful in removing spots of non-polar substances such as fuel oil, tar, or grease, but in this case a non-polar solvent (e.g., white spirit) must be used as the liquid phase [1,16].

Poultices must retain water to a certain extent to regulate the water evaporation velocity. They should also have high specific surfaces and a high ion exchange capacity to adsorb salts. In most cases effectiveness of salt extraction is higher for poultices containing clay minerals than for those containing only cellulose fibres.

Poultices based on clay minerals are advantageous because they don't need a daily check, which is necessary for cellulose containing poultices to prevent mouldiness. On the other hand, poultices made up of cellulose fibres have advantages: on fragile surfaces they are the first choice because they are soft, easy to handle and because they can be removed from most surfaces without residue.

Poultices can be distinguished based on two different principles which define how they work: wet and drying poultices. In this thesis wet poultices have been used, due to their predisposition to desalinize porous materials. This method is based on the

transport of soluble salts from the material into the poultice which is then removed with its salt content.

In wet poultices, water is a crucial element as it acts as transport medium. The transport can be distinguished in:

- Ionic diffusion of salts which is driven by the concentration gradient between the high salt concentration region of the substrate to the salt free water in the poultice.
- Salt in aqueous solution can also be moved by capillary transport of the solvent water. Capillary transport is possible in pores with radii between about 50 nm and 100 μm . It depends on the water content and the pore structure of poultice and substrate.
- Convective transport of aqueous salt solutions can be caused by gravity, external pressure or differences in density or temperature. This kind of transport preferentially takes places in large pores [1].

Once applied, the poultice is usually covered with a plastic or aluminium sheet to avoid the evaporation of the water and is left in contact with the surface to be cleaned for several hours determined after a series of tests (fig.7).

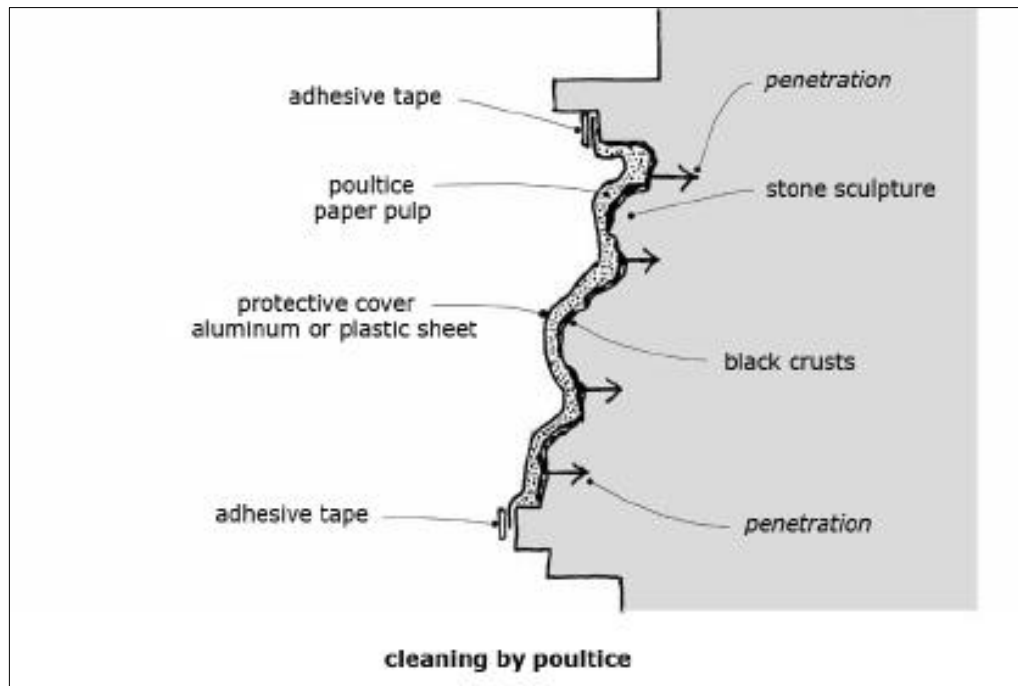


Figure 7 Poultice cleaning procedure [16].

When the protective sheet is removed, poultices are left on the surface until they are dry, as this helps draw out of the pores the saline solution. After the water evaporation, the dry material is carefully removed and disposed of [16].

EFFECTIVENESS OF SOLUBLE SALTS EXTRACTION BY POULTICE

It is essential to know the salt distribution in an object before taking a decision on the use of poultices. It must be noted that salt reduction perpetrated by poultices application usually affects the subsurface zone of porous stone material that measures only few centimetres. As a consequence, the optimum degree of cleaning can only be achieved if most of the salt is concentrated near the surface and if salt supply from adjacent zones is denied [1]. While the quantification of the amount of salts within a stone sample is rather simple, there are no appropriate non-invasive methods for accurately quantifying the distribution and the total amount of soluble salts in the entire material and in real situations. As lower regions of a wall will have different types and concentrations of salts in respect to upper portions; in the same way, differences can also be observed from the exterior wall surfaces to the interior of the walls. Due to these problems, the effectiveness of salt removal methods can only be estimated [10]. To enhance the soluble salts extraction, an electrochemical method has been recently proposed, described below.

SOLUBLE SALTS EXTRACTION BY ELECTROCHEMICAL METHODS

Electrodes are electric conductors generally made by metal or graphite whose purpose is to act as a bridge between the electrical circuit and a non-metallic component like a semiconductor, electrolyte or in our case: the poultices.

When used in an electrolytical context, an electrode can work as an anode or a cathode, depending on the reaction occurring. The electrode that hosts an oxidation reaction is called anode while the one hosting a reduction reaction is called cathode. When the motion of ions is caused by a difference in electrical potential between two electrodes in a solution, it refers to "migration", corresponding to the simultaneous movement of charges transport of both negative charged ions (anions) towards the cathode and positive charged ions (cations) to the anode.

In conservation field, desalination by electro migration has been proposed as a non-destructive method for extracting salts where the electrodes with an electric potential are inserted into a poultice situated on the surface to be cleaned.

The speed of the desalination process depends on the material properties and the potential applied [10].

ELECTROMIGRATION LIMITS

The electrokinetic techniques have two main limitations that can influence the movement of ions during the procedure:

- High quantity of H^+ and OH^- are produced from the water dissociation during the treatment by oxidation and reduction at the electrode respectively and flow in the medium to be treated.
- The different drying process that occurs at one of the electrodes: the drying restricts the flow of electric current through the material, thus reducing the total operating time of the system.

Variation in pH values during the treatment must therefore be kept under control because major variations could be responsible of chemical reactions with the stone material. Due to electrolysis, pH variations occur near both anode and cathode's surface. The presence of anions other than Cl^- will decrease the fraction of current transported by chlorines (transport number), which result in decreased efficiency of the extraction procedure with respect to Cl^- . In the related study [13], an experimental setup (fig.8) was designed to simulate real conditions in vaults and with ion contents corresponding to normal heavily polluted church vaults (1.0 wt.% Chloride, added as NaCl). The acid and base produced at the electrodes during the treatments due to electrode reactions determined significant pH changes and lack of proper desalination. A calculated amount of buffer poultices to reduce the pH variation and to optimize on the effects of desalination was proposed. For the neutralization of the produced H^+ at the anode, carbonate can be used. During reaction between $CaCO_3$ and acid (H^+), $CaCO_3$ decomposes ($CO_2(g) + H_2O + CaCO_3 = Ca^{2+} + 2HCO_3^-$) and gives the ability to oppose changes in pH.

For the neutralization of OH^- , Acetic acid (CH_3COOH) was used instead to oppose the OH^- formation at the cathode.

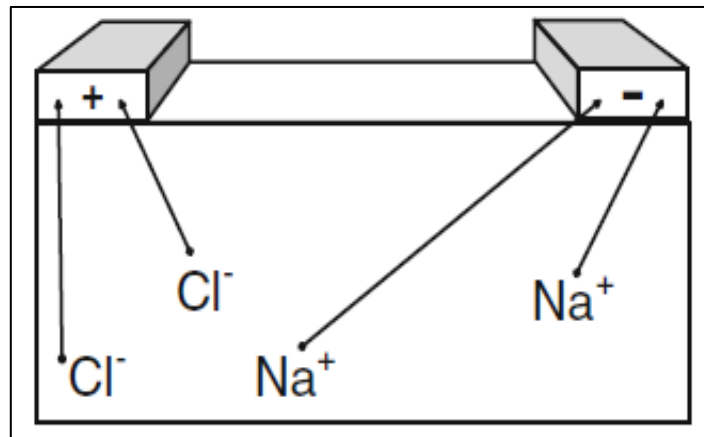


Figure 8 Experimental setup for desalination in Rörig's research [13].

In this setup, two electrodes are placed on the upper side in each end of the sample. Both electrodes are immersed in a kaolin poultice, which was chosen for the investigations due to its purity, low shrinkage, good workability, and conductivity when distilled water is added. As the treatment proceeds, salt (NaCl) will dissociate in Cl^- and Na^+ . At the anode by the reaction, $\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$, Cl^- in its vicinity is most likely to react and produce CaCl_2 . Instead, the Na^+ near the cathode by the reaction of $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$, will react and produce NaCH_3COO . In some initial experiments the exact amount of calcium carbonate was not sufficient to neutralize the calculated acid, and this could be due to a non-ideal behaviour of the buffer or to the physical placement of the electrodes. Both the anode and cathode are placed on the same side of the sample; therefore, the current distribution is non-uniform, and will result in a non-uniform consumption of buffer component. The use of acetic acid provided a high desalination effect and shown its limitation in use of solely neutralization at the cathode as diffusion of the acid occurred and lowered the pH in the substrate until equilibrium conditions were met. Later research by Rörig-Dalgaard [14] reports further development of the previous setup where cathode poultice from a single layer [13] was modified into a three-layered poultice. This was aimed to neutralize the H^+ production at the cathode, ensure precipitation of the buffering

agent in the cathode poultice while still maintaining a high desalination rate. Four poultices were produced, first poultice consists in kaolin clay and distilled water named “K” while second poultice made for neutralization of acid consists of kaolin clay, calcium carbonate and distilled water, named “Ca”. A third poultice named “Ci” for neutralization of base composed of kaolin clay mixed with citric acid was made (fig.9).

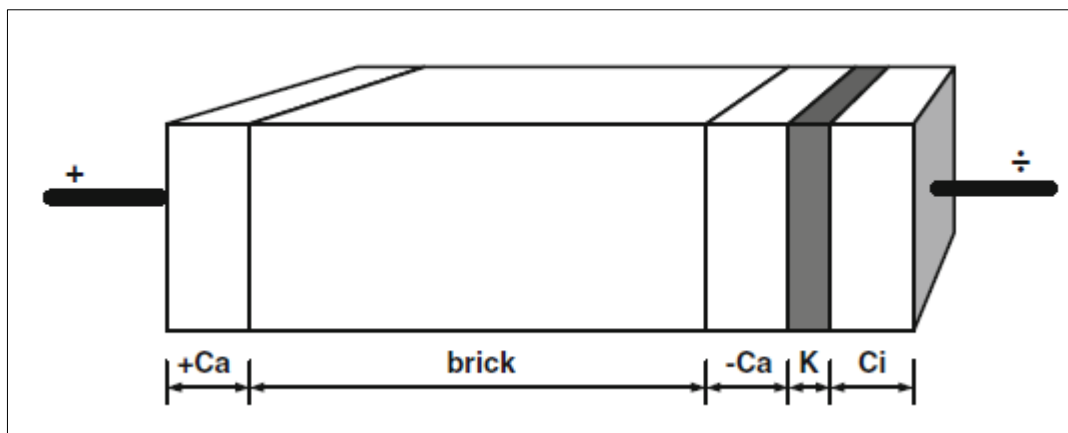


Figure 9 Improved model of Rörig's research [14].

As the Treatment proceeded, the following reactions were observed:

- “Ca”: $C_6H_8O_7(aq) + CaCO_3(s) = Ca_3(C_6H_5O_7)_2(s) + 3CO_2(g) + 3H_2O(aq)$;
- “K”: no reaction;
- “Ci”: $C_6H_8O_7(aq) + OH^- = C_6H_7O_7^-(aq) + H_2O(aq)$;

The development of the three-layered poultice cathode unit allowed to neutralize the electrochemical induced acidification with a citric acid which then precipitates in form of calcium citrate inside the cathode poultice avoiding variation of pH in the substrate. The precipitation of calcium citrate within the cathode poultice prevented also new ions to enter the substrate during the desalination. Through pH measurements and SEM observations it was shown that significant changes in the material occurred during the treatment just as a mortar crumbled when the cathode poultice was placed in contact with lime mortar. In addition, acetate ions entered

the material during the desalination of the original ions [14]. The double-anode-cathode setup (DAC) is an improvement of the standard electrode system [9]. It concerns the use of two cathodes and two anodes, whose setup is described below (fig.10), all the electrodes used were made of titanium-MMO mesh (titanium coated with mixed metal oxides) because of its inertness against oxidation reactions.

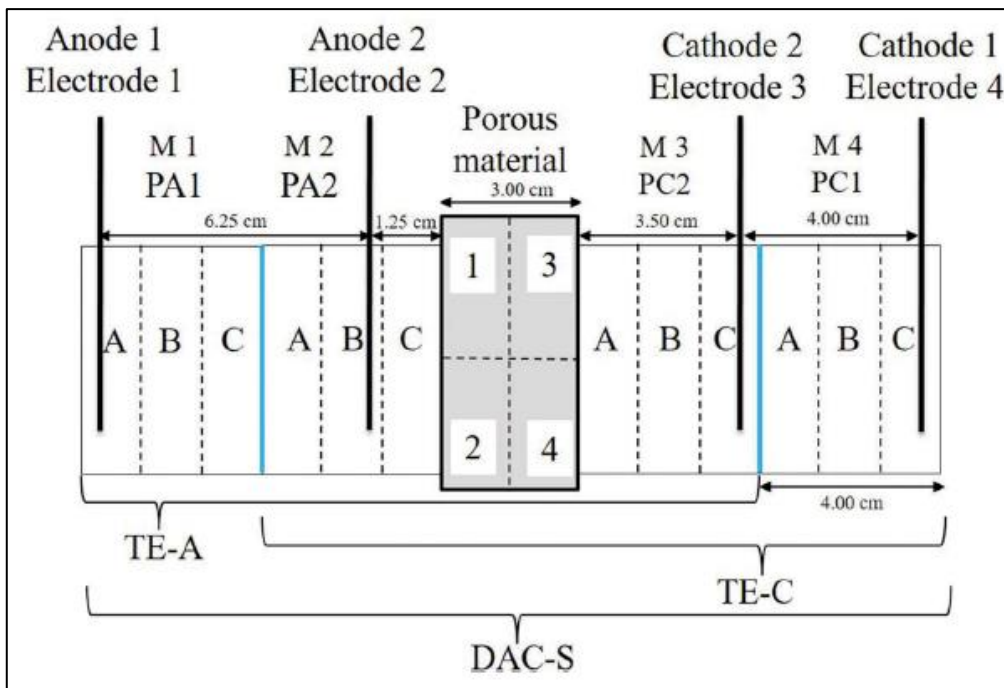


Figure 10 DAC setup diagram [9].

In the DAC system setup, medium M1 is filled with a poultice composed of cellulose and with an electrolyte of citric acid and sodium citrate buffered at pH 6 in a weight ratio of 1:7.6. M2 is filled with a poultice composed of kaolin, calcium carbonate, and citrate/citric acid electrolyte buffered at pH 6 in a weight ratio 1:2:1.3, respectively. These two media constitute the anodic compartment while the cathodic one is composed by M3, a poultice filled with kaolin and citrate/citric acid electrolyte buffered at pH 6 in a weight ratio of 1.6:1 and M4 was filled with a poultice (PC1) made of kaolin, calcium carbonate and citrate/citric acid electrolyte buffered at pH 5, selected to favour the dissolution of

calcium carbonate by precipitation of $\text{Ca}(\text{OH})_2$ produced by calcium ions reacting with OH^- ions (fig.11).

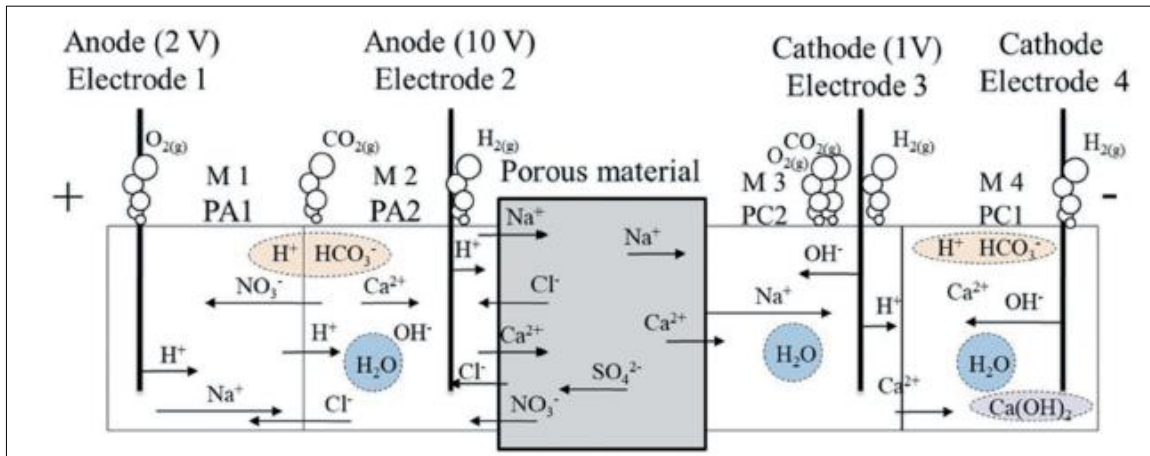


Figure 11 DAC diagram for active species during desalination [9].

The research by Feijoo [9] was focused on improving the pH buffering capacity at the anode and increasing the effectiveness of the conventional desalination treatment due to reduction of the H^+ concentration in the proximity of the stone to be treated. On the other hand, alkaline pH values were observed at the cathode in different studies as a limit to the application of this setup. The treated material could be in fact damaged by low acidic pH values coming from the anode and the probable entrance in the material of high OH^- ions produced meanwhile at the cathode could reduce the effectiveness of the treatment [9].

The present thesis focuses on evaluating the behaviour of a new electrokinetic system configuration in respect to water content, pH buffering and system requirements. This new double electrode system implies the use of a total of four electrodes, two acting as anodes and two as cathodes. These electrodes will surround the artificially salted sample, using poultices that will act as a medium for ions to flow in during extraction. Different EC values will be applied to test the effectiveness and various configurations will be tested while the values of pH and conductivity will be analysed for each experiment to carry out which is the best configuration.

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2. MATERIALS AND METHODS

Some drawbacks of traditional electrode-based techniques related with the mobilization of salt ions and with the porous material integrity due to the possible chemical and/or aesthetic damages had still to be overcome. In this study the first setup had to be modified to be fully operational. The electrode-based model was inspired by a double anode-cathode system evaluated in a previous case of study [3], based on two electrodes immersed in poultice medium per compartment, anodic and cathodic, called DAC (Double Anode Cathode).

The DAC model setup allows:

- Maintaining a high-water content in the stone and the poultices which results in a good ionic contact between electrode-poultice-stone.
- The water content of the setup allows maintaining higher operation currents, which increases ion transport.
- Stabilization of pH values, thus minimizing chemical alteration of sample.
- More homogeneous and efficient ion mobilization, which enables to reach high percentages of ion extraction and the residual ion concentration remaining is symmetrical (anode and cathode sides) with the DAC-S setup.

To overcome the limits that the desalination treatment has shown, some deep studies have been done on other papers that focused on a similar topic. The acidification at the anode is an issue which is often found in electrode cleaning procedures, different cases of study concerning electrochemical desalination have pointed out multiple solutions to solve or limit the problem:

- Exploiting the fact that acidic front develops very slowly when in calcareous soils, the presence of a certain carbonate

quantity in the poultice prevents the acidification during the treatment. [4][5][7]

- As the salts concentrate in the poultice during the treatment, it's possible to remove salts from the artifact at the end of the treatment by removing the clay. [5]
- Sample conductivity is important to maintain a good ionic contact with the poultices. Dry samples must be moisturized with small quantity of water to enhance ion mobility. Soaking must be therefore avoided because it would mean wash off efflorescences and surface near salts. [4]

The first model was a simplification of the original DAC system [3]. The complexity of the build was changed in a vertical succession of layers and electrodes, utilizing water to produce sepiolite and cellulose pulp poultices, and using titanium flat grid electrodes (5x15cm) for the electrical part.

Sepiolite is a fibrous clay mineral composed of discontinuous structural parts alternated with structural tunnels. Each block has a 2:1 phyllosilicate structure, which is made by a central octahedral sheet between two silica tetrahedral sheets Si-O-Si bonds [1,2]. Due to Kaolin tendency to leave white deposits on the stone [3] sepiolite was chosen instead, its high absorption capacity has made it a material of frequent use in the Cultural Heritage cleaning field; upon wet application, this facilitates the salts dissolution within the stone material and migration of ions to the outside, where they recrystallize and are retained [2]. The Cellulose pulp, also known as paper pulp, is a pure cellulose fiber that swells in water without dissolving. It easily retains water solutions mixed with detergents or other chemical products. It's an acid and weak alkali resistant material often used to create poultices in restoration treatments. [6] It has a high liquid storage capacity but no pH buffering capacity, which allows, if not prevented, a large amount of H⁺ ions to be generated near the E1. [3]

The first setup therefore suffered from different problems, mainly related with pH variations and the dry up of the poultices. The deionized water used for the poultices would undergo electrolysis, thus causing the H^+ production at the anode (fig.12).

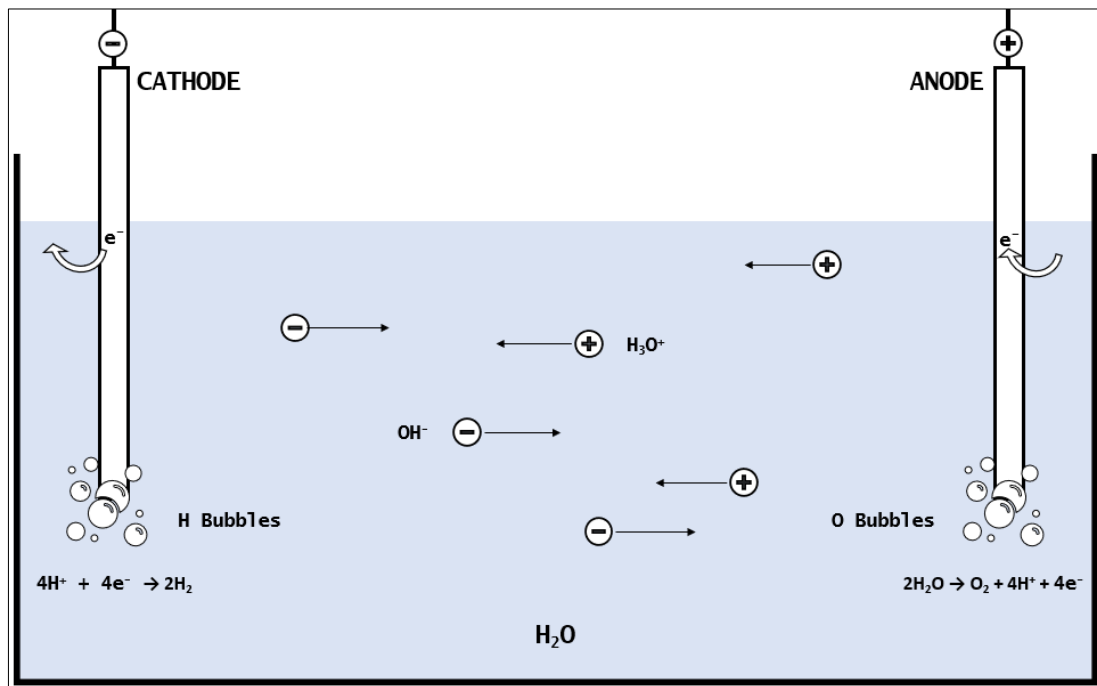


Figure 542 Electrolysis of water.

These problems caused the desalination process to stop prematurely. Due to wires composition that was not pure titanium and pH induced corrosion, the metal inserted in the electrodes would degrade and break, interrupting the electric current flux (fig.13).



Figure 123 Acidification damages to the Ti wires.

The newest electrode system was created in the laboratory, modifying parts of the previous build in order to increase the treatment's durability and sample protection. The improvements made in the system were specifically:

- Substitution of electrode's metal wiring with a titanium one due to its high corrosion resistance.
- A new poultice system has been produced; magnesium citrate was added to the poultices as buffer to prevent pH variations.
- An automatic irrigator was chosen to moisturize the setup during the treatment.
- The whole setup was re-dimensioned, using polystyrene blocks to reduce the amount of material used for each experiment.

With the final system assembled, multiple treatments have been executed, using artificially salted bricks and Vicenza limestone. Each electrode-based treatment was paired with a simple poultice treatment, without electrodes, whose layer setup was the same as the electrode system.

2.1. ELECTROCHEMICAL SYSTEM DEVELOPMENT

The electrical circuit of the global system was left untouched during the enhancements (fig.14). Four flat grid titanium electrodes called E1, E2, E3 and E4 (16,5x4,5cm each) were linked to three HANMATEK 5A-30V generators; E4 was linked at generator 3-4 with a 1k Ω resistor. The three power sources are called “1-2”, “2-3” and “3-4” (referred to the electrodes with which they are connected), their electric potential had been set respectively to 2V, 10V, 1V like in previous literature [3] (fig.14).

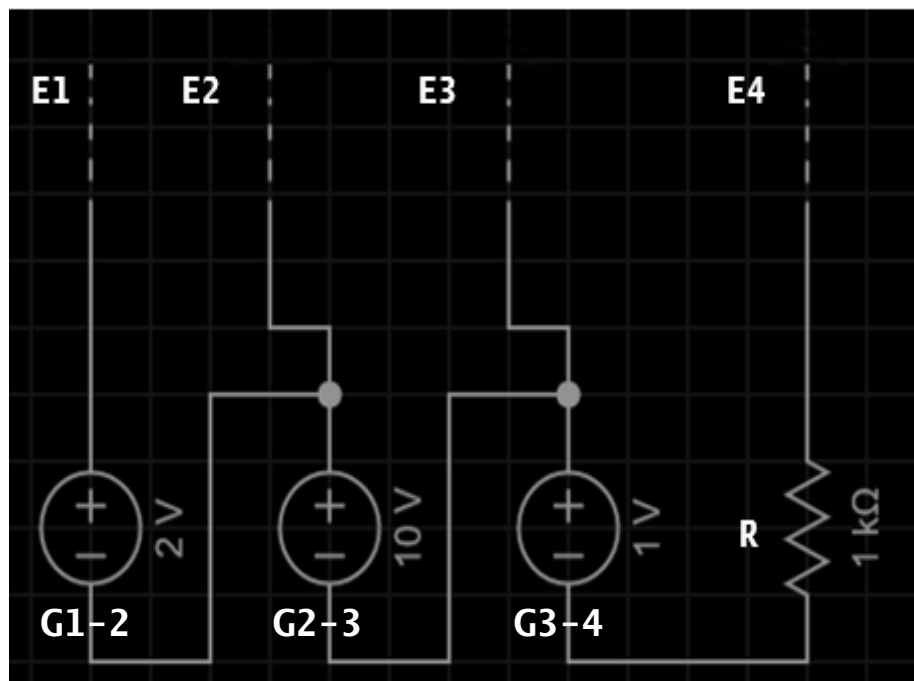


Figure 14 Electrical circuit diagram for the electrochemical system.

Different voltages were experimented during this research, increasing generator 2-3 electric potential's from 10V to 16V and to 20V to evaluate the difference in salt extraction capacity with different potentials. A FLUKE multimeter, linked to the resistor, was used to measure the ac+dc current value during treatments, and the display of the generators to read the electric current values for Volt/Ampere/Watt, also critical to determine the progression of the treatment.

2.2. BUFFER SOLUTION

In the study by Feijoo [3] the buffer action was achieved by different poultice compositions made by citric acid and sodium citrate for the cellulose layer and kaolin, calcium carbonate, and citrate/citric acid, both buffered at pH 6, for the other layers. This composition was simplified by adopting a single buffer solution that had to be used when mixing the cellulose pulp and the sepiolite in their respective sections. The pH buffer consisted in a solution of magnesium citrate ($C_6H_6MgO_7$) (fig.15).

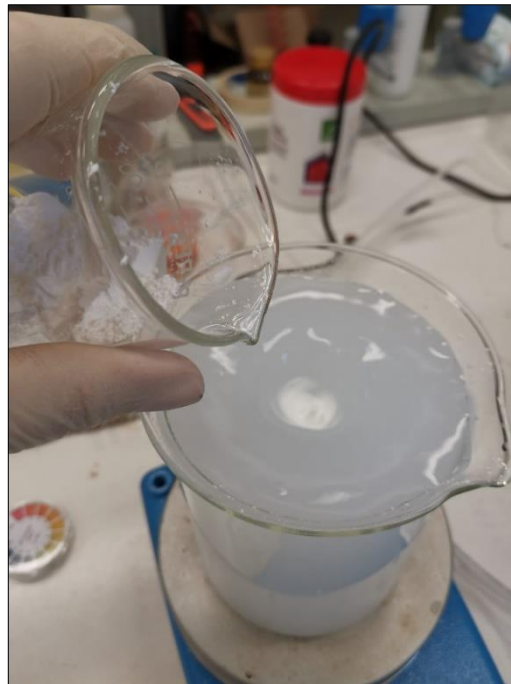
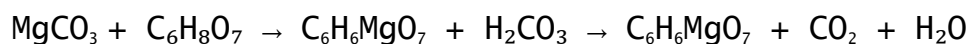


Figure 15 Buffer solution production.

This was produced by dissolving in a deionized water solution, anhydrous citric acid, and magnesium carbonate. The three components in a weight ratio 1:0,038:0,025.



From the reaction between citric acid and magnesium carbonate, magnesium citrate and carbonic acid are produced, which dissociates in H_2O and CO_2 . After all the magnesium carbonate has been dissolved and the CO_2 bubbling stopped the solution is buffered at pH 7 and assumes a whitish tint, meaning that the magnesium citrate buffer was ready to be mixed in the poultices.

2.3. POULTICE SYSTEM

For the poultice system, sepiolite and cellulose pulp have been used. For each type of layer, a determined quantity of solid product has been mixed along with the liquid: 1000g (l):800g(s) for sepiolite layers and 200g(l):100g(s) for the cellulose pulp layer. The setup was built vertically, putting the anodic part at the top and the cathodic at the bottom. Each electrode is inserted in the middle of its section of poultice which is separated from the other with an unwoven tissue sheet to avoid poultices mixing and to facilitate the detachment of layers from the material after the treatment.

The setup is composed by the bottom cathodic section, made respectively by two sepiolite layers, on whose surface a sheet of unwoven tissue has been placed. The central part is occupied by the sample. The top anodic part begins with a sepiolite layer and the uppermost cellulose layer, and each electrode has been inserted in the middle of its section.

The sepiolite poultices were produced by mixing the solid material with magnesium citrate buffer in ratio 1:1,25 in order to obtain a highly moisturized pack that would favourite the ion movement during the treatment.

The cellulose pulp layer was mixed instead with smaller quantities of buffer, due to the high hygroscopicity of the material, and the resulting poultice was only slightly deprived of excess water before being punt on the previous layer. The

final setup had a minor variant, where two 5mm CaCO_3 layers had been inserted as ulterior sample protection feature right below and above the sample (fig.16).

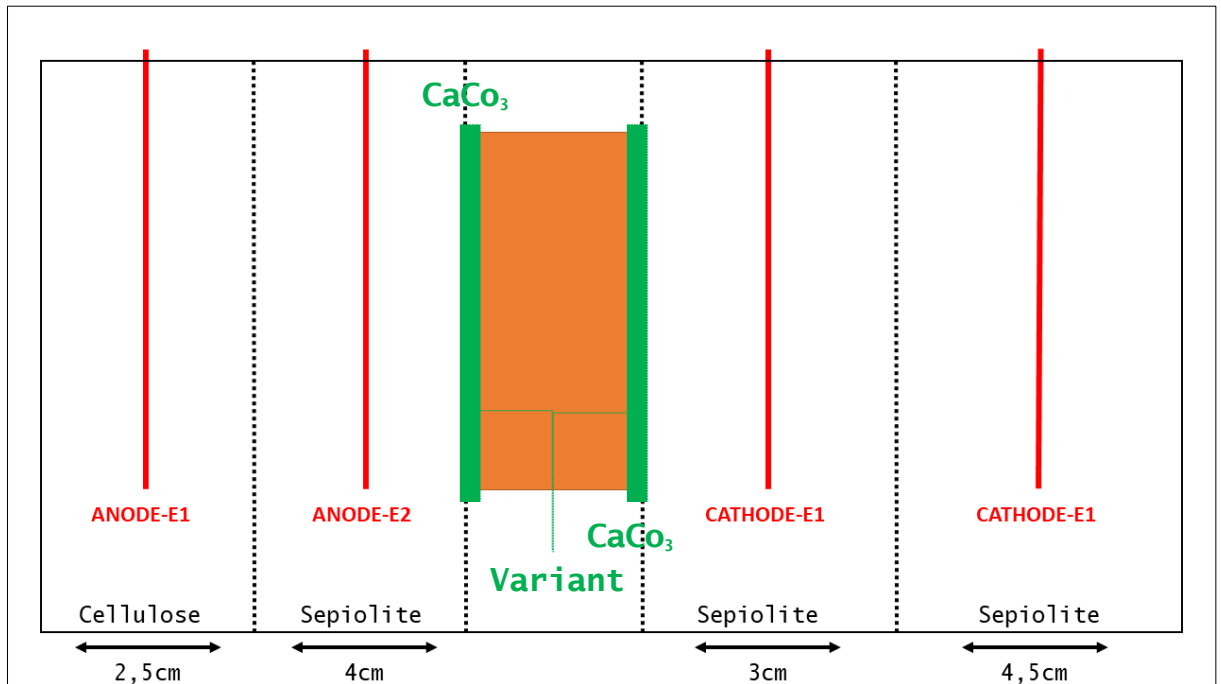


Figure 16 Diagram for electrode-based poultice setup layers.

2.4. SAMPLE PREPARATION

To verify the actual efficiency of the desalination procedure, different specimens have been prepared. First experiments focused on bricks desalination then of carbonate stones (Vicenza stone). The bricks (San Marco Terreal) were first cleaned of the dust with brushes, then weight was written down right before immersion in a large plastic container filled with oversaturated NaCl salted water solution (fig.17).



Figure 17 Samples immersed partially in NaCl oversaturated solution.

During the first experiences, before the assembling of the final electrode setup, the bricks were salted through immersion but, in order to reduce the amount of tap water used and to simulate real cases specimens and to increase the amount of salt content, the capillarity method was chosen instead. The Vicenza stone tiles, were cleaned in the same way, using brushes, and then they were artificially salted by immersion in a few inches of oversaturated salt water. Each sample has undergone multiple cycles, alternating 1-day of imbibition with a 12-hour stove cycle. The samples analysed during this experience had different sizes, three bricks: 2,3,13,16,20 (25x12x3cm), smaller bricks 4,6,7,8 (8,5x12x3cm) and carbonate samples, LGL, 2, VG4 and NG5 (both 4,5/12/1,5cm in dimensions).

2.5. EVALUATION OF THE EFFECTIVENESS OF THE METHOD

During this experience, different methods for the evaluation of the desalination treatment efficiency and setup condition control have been used:

- A CRISON GLP 31 desk conductometer with a Pt conductivity cell was used to measure conductivity. Conductivity (σ) is measured in Siemens/centimetre (S/cm). Through a 5mm diameter drill a hole is dug up to 5mm deep inside the bulk material after and before the treatments. The sampling of carbonate tiles was less invasive, due to the smaller dimensions of the specimen. The powder is then collected and put in stove to dry. After a half-hour in stove the powder is ready to be weighed. 100mg of material are put inside a clean container and then 100ml of deionized water are added, following the UNI-Normal indication [4]. The soluble salt solution is left to rest for a day, then it is ready to be measured with a conductometer. Before each EC measurement, the system must be calibrated with appropriate standard solutions (fig.18).



Figure 18 CRISON GLP 31 desk conductometer.

- The pH values needed to be controlled throughout the treatments in order to determine the variation of H^+ and OH^- in the poultices. Litmus paper was used jointly with a Mosthink Multimeter with two sensors that had to be inserted deep in the material to measure pH value. Two pair of holes have been made in the plastic container at height corresponding with each poultice layer. This allowed to get a proper reading of pH during the treatment for each layer (fig.19).



Figure 19 Holes in the container to allow pH measurements.

During each treatment a couple of stone materials of the same nature were selected, with similar conductivity value, and put in a different setup, the electrochemical system (EC) or the diffusion system (DF) in order to evaluate the effective efficiency of the electrode-based system in confront to the traditional procedure.

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3. RESULTS AND DISCUSSION

3.1. BRICK DESALINATION

The first experience focused on evaluating the minimal amount of Voltage to start the desalination treatment. On this experiment the Voltage of generators 1-2 and 3-4 were set respectively to 2V and 1V, meanwhile the treatment the voltage of generator 2-3 was progressively increased, starting from 0.33V to observe the variation of pH related to Voltage.

Through the application of a certain potential difference at the electrodes 2 and 3, the ones surrounding the sample, an increase in wattage and amperage of electrodes 1 and 2 is achieved (tab.2).

Table 2 Electric values for Voltage test experimentation.

Time (h)	A 1-2	W 1-2	V 2-3	A 2-3	W 2-3	pH (From top layers)
0,000	0,000A	0,000W	0,330V	5,100A	1.683W	5.5/6.5/8/8
5,500	0,000A	0,000W	0,340V	5,100A	1.732W	5.5/6.5/8/8
7,000	0,000A	0,000W	0,370V	5,100A	1.885W	5.5/6.5/8/8
24,500	0,000A	0,000W	0,500V	5,100A	2.550W	5.5/6.5/8/8
25,000	0,000A	0,000W	0,500V	5,100A	2.550W	5.5/7/8/8
26,000	0,0390A	0.078W	10,000V	4,800A	0.480W	5.5/6/8/8
32,000	0,0740A	0.148W	10,000V	0,860A	0.086W	4/4.5/7/8

Upon reaching 10 Volts the desalination process starts as the ions within the system are extracted from the substrate by the influence of induced ion flux. When all ions have been removed, the sample will not be able to conduct electric current, so the treatment reaches the stop. Following is a tab.3 showing the electrical values of sample "20", which did not undergo saline treatment, in order to show how the ion flux is influenced by the presence of conductive species within the specimen.

Table 3 Electric values for sample 20 (no salt content).

Time (h)	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
0,000	0,002	0,004	0,010	0,195	1,460
0,100	0,001	0,002	0,009	0,144	1,430
0,100	0,000	0,000	0,009	0,144	1,400
0,200	0,000	0,000	0,008	0,128	1,380
0,200	0,000	0,000	0,008	0,128	1,360
0,300	0,000	0,000	0,007	0,114	1,340
0,300	0,000	0,000	0,006	0,096	1,320
0,300	0,000	0,000	0,006	0,096	1,300
0,400	0,000	0,000	0,005	0,080	1,290
0,600	0,000	0,000	0,000	0,000	1,130

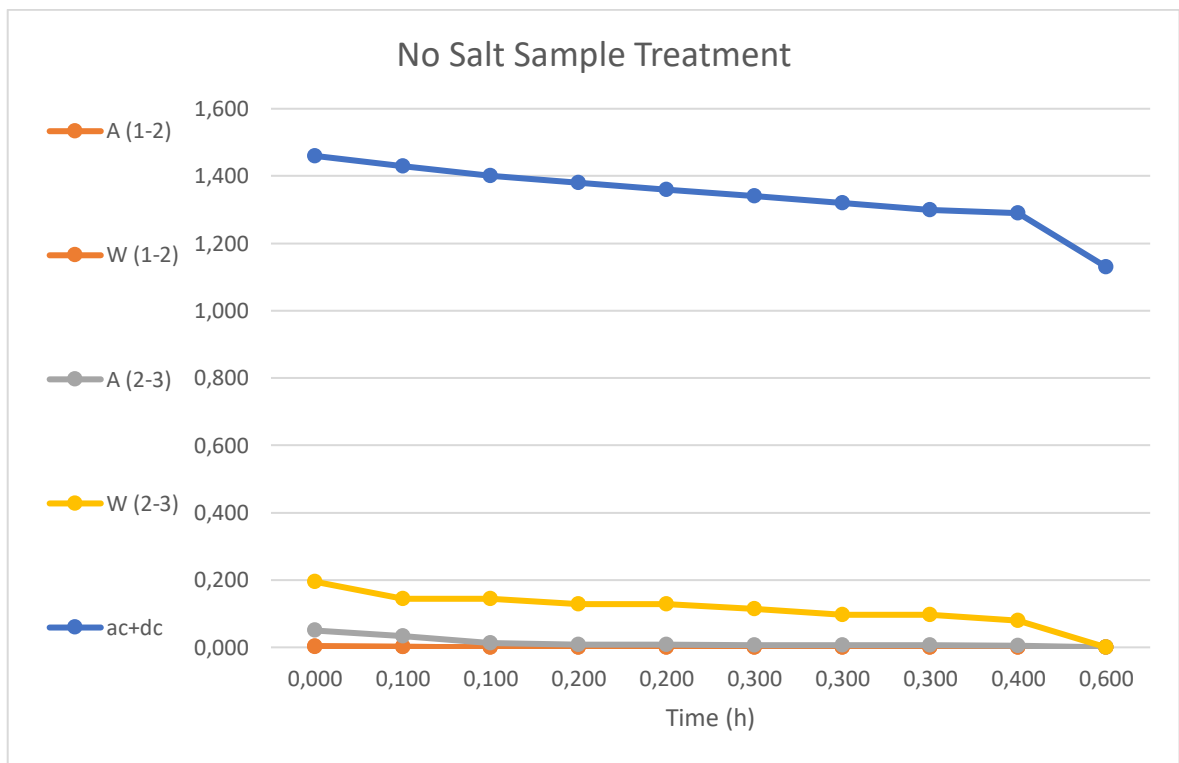


Figure 20 Progression curve for sample 20 treatment.

It's clear that the absence of conductive species inside the sample doesn't allow the treatment to work properly, as the current is not flowing between the anodes and it's minimal in the rest of the system. As a fact, the values for A1-2 and W1-2 never reached values different than 0, except for the highlighted moments in fig.20 where an extra of 30ml of buffer solution was added. This made clear that the content of salt inside a porous material is necessary to run the treatment,

the presence of these conductive species allow the electric current to flow through all the setup, passing through cathodes, sample and anodes extracting the salt ions. The 10 Voltage of generator 2-3 (tab.2) sets the start for the treatment but it determines a reduction in the anodic pultices pH, which has been already observed as one of the reasons why electrochemical methods necessitate CaCO₃ layers and buffer solutions to work properly, especially to avoid damages on carbonate supports. The results have shown that, at low Voltage values, the pH does not seem to suffer from the H⁺ and OH⁻ production at the electrodes. This made clear that, as high Voltage is required in order to start the desalination, a pH buffering system was needed to reduce the acidification phenomenon.

After the production of magnesium citrate solution, the first bricks treated were sample “2” in the electrochemical system and “3” in the traditional diffusion system, the following tab shows the treatment progression’s electrical values in the first 4 hours (tab.4).

Table 4 Electric values for sample 2 treatment.

V1-2 [2V]	V2-3 [10V]		V3-4 [1V]		
Time (h)	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
0,000	0,057	0,114	0,064	0,640	1,640
0,100	0,054	0,108	0,063	0,640	1,640
0,200	0,050	0,100	0,062	0,620	1,630
0,300	0,048	0,096	0,060	0,600	1,620
0,400	0,046	0,092	0,058	0,580	1,620
0,500	0,045	0,090	0,055	0,550	1,610
0,800	0,042	0,084	0,053	0,530	1,600
1,000	0,040	0,080	0,051	0,510	1,590
1,500	0,036	0,072	0,048	0,480	1,580
2,000	0,033	0,066	0,045	0,450	1,580
2,200	0,030	0,060	0,042	0,420	1,570
2,300	0,026	0,052	0,038	0,380	1,570

2,400	0,023	0,046	0,035	0,350	1,560
2,500	0,035	0,064	0,049	0,490	1,560
2,600	0,021	0,042	0,033	0,330	1,550
2,700	0,017	0,034	0,026	0,260	1,550
2,800	0,012	0,024	0,021	0,210	1,550
2,900	0,009	0,018	0,012	0,120	1,540
3,000	0,005	0,010	0,010	0,100	1,540

Through the irrigation system, buffer solution was provided to the two setups, increasing the durability of the system up to 19 hours straight (fig.21); the highlighted points are referred to the extra add of 30 ml of buffer solution, that caused an increase of electric current values, in particular for wattage.

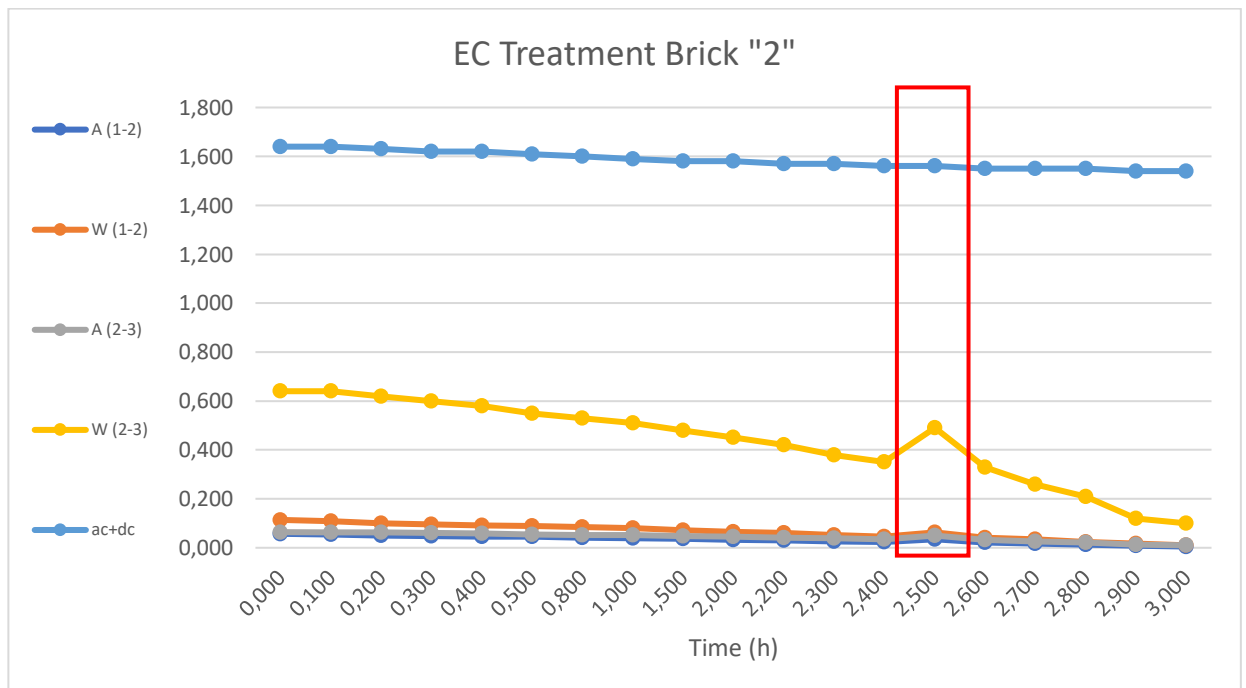


Figure 21 Progression curve for sample 2 treatment.

As the treatment proceeds (fig.21), the values for electric current intensity (A) and power (W) decrease rapidly over time; when low values are reached, the curve starts to slow its decrease. The setup was left working for 19 hours and stopped as the generators shown that no current was passing inside the system anymore. A good conductivity reduction was achieved in both cases (tab.5). The electrochemical system EC proved again to be slightly more efficient for desalination treatment as

the value for “ Δ CONDUCTIVITY%” is bigger than the one for diffusion treatment DC.

Table 5 Conductivity values variation for sample "2,3".

TREATMENT	SALT CYCLES	SAMPLE	COND. BEFORE (μ S/cm)	COND. AFTER (μ S/cm)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	2	164,7	51,2	68,9%
DIFFUSION SYSTEM (DF)	3	3	159,8	56,8	64,4%

The magnesium citrate buffer solution has proven to be a good countermeasure to pH variation, as the tab below (tab.6) shows the only layer who suffered a major variation was the cellulose one, but its position is far from the sample and the setup didn't go under further modification whatsoever.

Table 6 ph values in different layers.

LAYER	pH BEFORE TREATMENT	pH AFTER TREATMENT
CELLULOSE PULP	7	5
SEPIOLITE	8	7
CaCO ₃	7-8	8
CaCO ₃	7-8	8
SEPIOLITE	8	8
SEPIOLITE	8	8

Similar results were achieved with samples “4” and “6”, which were produced from a brick sawn in three pieces. In the following table (tab.7), the progression of the electric current values is shown. Like the previous experience, the electrode-based system was paired with a diffusion system, for this treatment: sample of brick “4” was put inside the diffusion system while “6” in the electrochemical one.

Table 7 Electric values for sample 6 treatment.

	V1-2 [2V]	V2-3 [10V]		V3-4 [1V]	
Time (h)	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
0,000	0,064	0,128	0,076	0,760	1,650
0,100	0,061	0,122	0,075	0,750	1,640
0,100	0,059	0,118	0,074	0,740	1,640

0,200	0,058	0,116	0,073	0,730	1,630
0,200	0,056	0,112	0,072	0,720	1,630
0,300	0,054	0,108	0,071	0,710	1,620
0,500	0,051	0,102	0,070	0,700	1,620
0,700	0,051	0,102	0,067	0,670	1,610
0,800	0,048	0,096	0,065	0,650	1,600
1,000	0,046	0,092	0,063	0,630	1,590
1,200	0,043	0,086	0,060	0,600	1,580
1,200	0,039	0,078	0,057	0,570	1,580
1,200	0,036	0,072	0,054	0,540	1,570
2,300	0,032	0,064	0,050	0,500	1,570
2,400	0,029	0,058	0,047	0,470	1,560
2,400	0,026	0,052	0,046	0,460	1,560
2,400	0,024	0,048	0,041	0,410	1,550
2,600	0,023	0,046	0,038	0,380	1,550
2,700	0,018	0,036	0,033	0,330	1,550
2,800	0,012	0,024	0,024	0,240	1,540
2,900	0,009	0,018	0,022	0,220	1,540
3,000	0,005	0,010	0,010	0,100	1,520

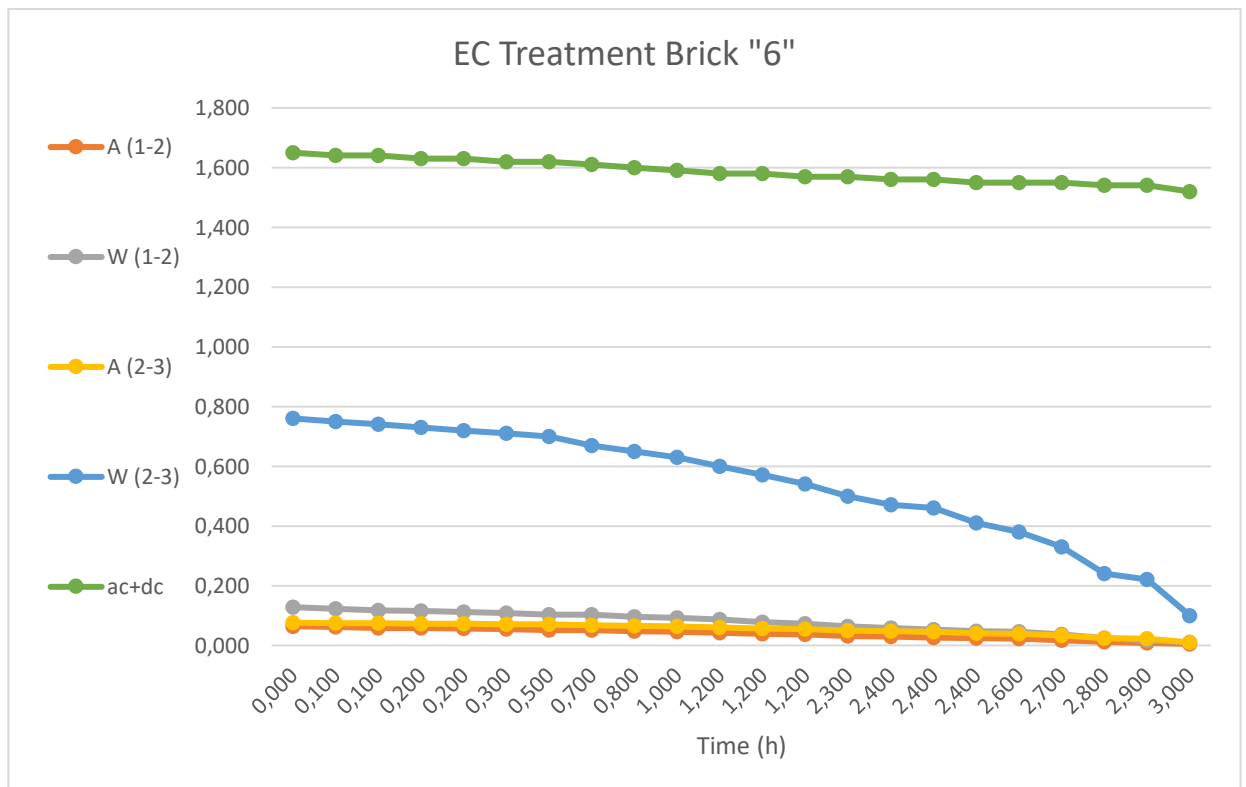


Figure 22 Progression curve for sample 6 treatment.

The previous graph (fig.22) shows the decrease over time of the Wattage and Amperage for brick "6", up to the point where no more conduction is possible. The conductivity values, measured after collecting powder by drilling from each sample, were reported before and after the desalination treatment, together with the variation in the conductivity (tab.8).

Table 8 Conductivity values variation for sample "4,6".

TREATMENT	SALT CYCLES	SAMPLE	COND.BEFORE ($\mu\text{S}/\text{cm}$)	COND.AFTER ($\mu\text{S}/\text{cm}$)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	4	137,3	50,5	63,2%
DIFFUSION SYSTEM (DF)	3	6	127,4	54,7	57%

This experiment show that EC treatment resulted in lower reduction of the saline content, in comparison with DF method.

Table 9 pH values in different layers.

LAYER	pH BEFORE TREATMENT	pH AFTER TREATMENT
CELLULOSE PULP	6-7	6
SEPIOLITE	7-8	7
CaCO ₃	8	8
CaCO ₃	8	8
SEPIOLITE	8	8
SEPIOLITE	8	8

It's rather clear that the buffer solution contrasted the H⁺ ions at the anode, due to the cellulose pulp's high liquid storage capacity but no pH buffering property (tab.9).

The next treatment is characterized by a slight increase of potential difference in generator 2-3, in order to test the efficiency of the system, from 10V to 16V.

Samples of brick "7" and "8" were utilized for this treatment, in the Electrochemical system and Diffusion system respectively.

Table 10 Electric values for sample 7 treatment.

Time (h)	V1-2 [2V]		V2-3 [16V]		V3-4 [1V]	
	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc	
0,000	0,037	0,045	0,118	1,888	1,580	
0,100	0,060	0,118	0,105	1,680	1,570	
0,100	0,055	0,108	0,099	1,584	1,570	
0,200	0,038	0,076	0,107	1,712	1,550	
0,200	0,025	0,050	0,092	1,472	1,540	
0,300	0,024	0,046	0,090	1,440	1,560	
0,400	0,021	0,042	0,088	1,408	1,560	
0,500	0,017	0,034	0,086	1,376	1,550	
0,600	0,012	0,024	0,080	1,280	1,540	
0,700	0,011	0,022	0,080	1,280	1,540	
0,800	0,014	0,032	0,120	1,220	1,540	
0,800	0,011	0,022	0,105	1,190	1,590	
0,900	0,008	0,016	0,081	1,186	1,530	
1,100	0,007	0,014	0,074	1,184	1,520	
1,200	0,007	0,014	0,074	1,184	1,510	
1,200	0,007	0,014	0,073	1,168	1,510	
1,300	0,006	0,012	0,071	1,136	1,510	
1,500	0,005	0,010	0,069	1,104	1,500	
1,600	0,005	0,010	0,069	1,104	1,500	
1,600	0,005	0,010	0,067	1,072	1,500	
1,700	0,005	0,010	0,066	1,056	1,490	
1,800	0,005	0,010	0,064	1,024	1,480	
2,100	0,004	0,008	0,063	1,008	1,480	
4,100	0,000	0,000	0,051	0,816	1,470	
17,100	0,006	0,012	0,012	0,192	1,240	
20,100	0,006	0,012	0,011	0,176	1,240	
22,100	0,007	0,014	0,011	0,176	1,240	
24,100	0,006	0,012	0,009	0,144	1,230	
41,100	0,000	0,000	0,000	0,000	1,210	

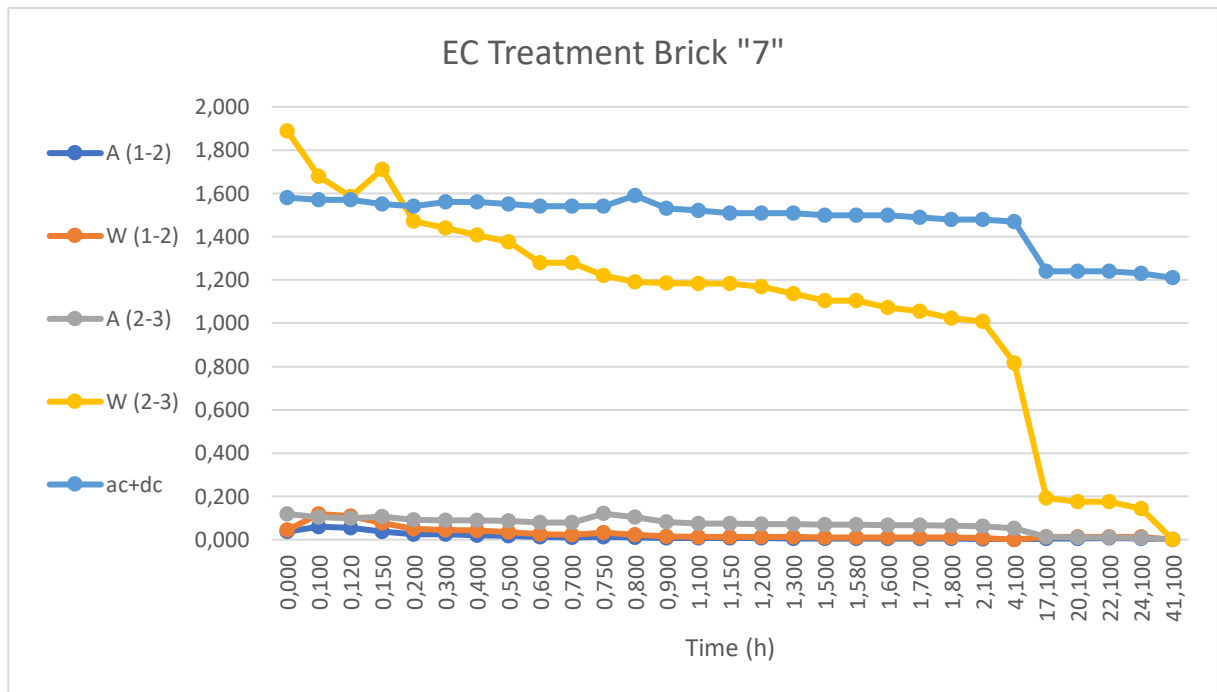


Figure 23 Progression curve for sample 7 treatment.

As the previous tests, the increase of Voltage from 10V to 16V does not create differences in the variation of Wattage and Amperage during the process (tab.10; fig.23).

As the tab below shows, the conductivity variation is lesser than in the previous experiments.

Also, the extra 7 hours duration of the process after reaching the first stop was achieved by adding a 30ml buffer solution to the system.

Table 11 Conductivity values variation for sample "7,8".

TREATMENT	SALT CYCLES	SAMPLE	COND. BEFORE ($\mu\text{S}/\text{cm}$)	COND. AFTER ($\mu\text{S}/\text{cm}$)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	7	177,6	150,7	15,1%
DIFFUSION SYSTEM (DF)	3	8	238	147,9	37,8%

The Conductivity variation seem to be limited to small percentages, probably due to the limited open porosity of the brick. At the same time the increase of Voltage seems to have not influenced the efficiency of the system.

Another last experimentation on bricks was done, this time changing the geometry of the electrodes: E1 at the top, E2

below E1 but above the samples and E3/E4 on the sides. Power supply 3-4 was not used. The resistor was put between power supply 2-3 and E3/E4, which were on the sides of the sample and connected via a wire. Sample “16” was put inside the EC system while sample “13” inside the DF system.

Table 12 Electric values for sample 16 treatment.

V1-2 [2V]		V2-3 [10V]		V3-4 [1V]	
Time (h)	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
0,000	0,011	0,022	0,012	0,192	12,910
0,100	0,011	0,022	0,011	0,176	12,900
0,120	0,011	0,022	0,011	0,176	12,500
0,130	0,011	0,022	0,011	0,176	12,500
0,160	0,010	0,020	0,011	0,170	12,300
0,200	0,011	0,022	0,010	0,160	12,100
0,400	0,010	0,020	0,009	0,144	11,900
0,500	0,010	0,020	0,009	0,144	11,800
0,600	0,009	0,018	0,009	0,144	11,600
0,700	0,008	0,016	0,009	0,144	11,500
0,900	0,008	0,016	0,009	0,144	11,500
1,000	0,007	0,014	0,009	0,144	11,400
1,100	0,007	0,014	0,009	0,144	11,300
1,200	0,007	0,014	0,009	0,144	11,200
1,500	0,007	0,014	0,009	0,144	11,100
1,600	0,007	0,014	0,008	0,128	11,000
1,700	0,007	0,014	0,008	0,128	11,000
1,750	0,006	0,012	0,008	0,128	10,900
1,760	0,006	0,012	0,008	0,128	10,800
1,800	0,006	0,012	0,008	0,128	10,600
1,900	0,005	0,010	0,008	0,128	10,600
2,000	0,005	0,010	0,008	0,128	10,500
2,100	0,005	0,010	0,007	0,112	10,300
2,500	0,005	0,010	0,006	0,010	9,700
3,000	0,005	0,010	0,005	0,080	8,450
5,000	0,004	0,008	0,005	0,080	8,200
15,500	0,000	0,000	0,005	0,080	8,000

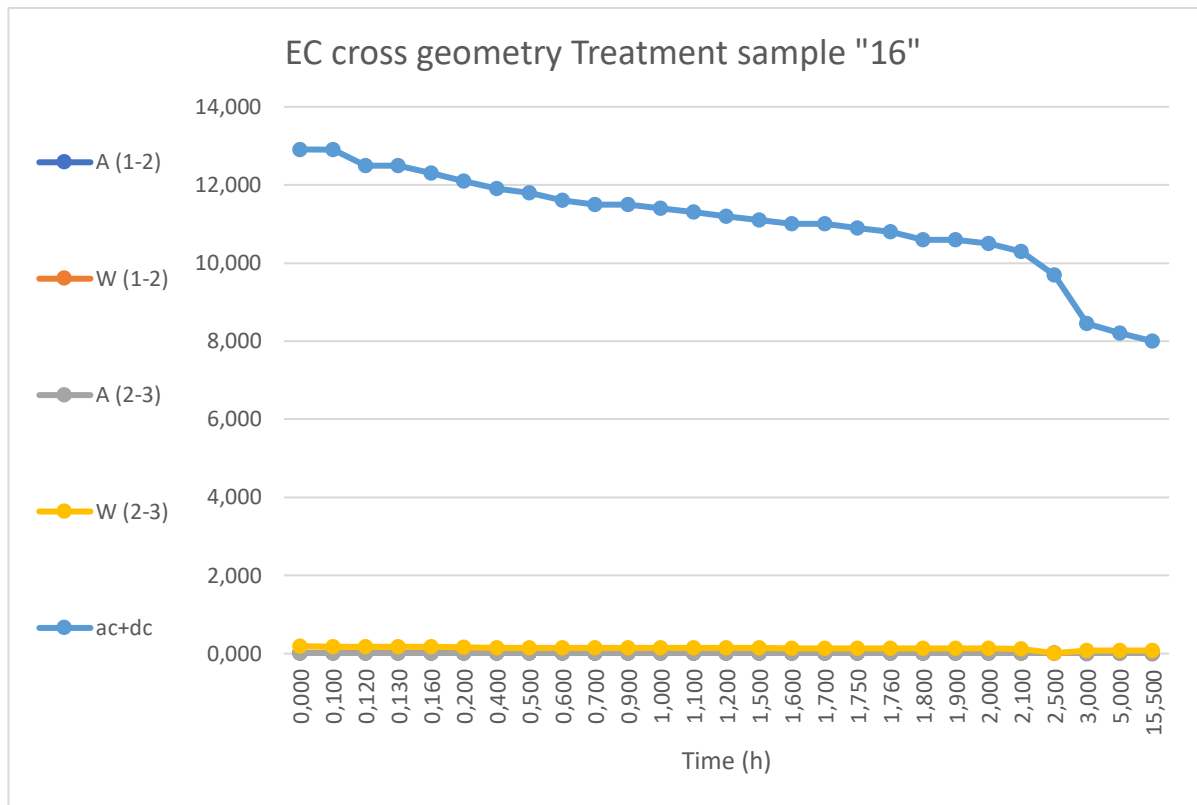


Figure 24 Progression curve for sample 16 treatment.

Due to the cross geometry, the influence of the potential difference on the layers is minimal. This made clear that the positioning of the electrodes in respect to the sample is highly important as it directly influences the strength of the desalinating ion flux (tab.13; fig.24).

Table 13 Conductivity values variation for sample "16,13".

TREATMENT	SALT CYCLES	SAMPLE	COND. BEFORE (μS/cm)	COND. AFTER (μS/cm)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	16	171,9	115,4	32,8%
DIFFUSION SYSTEM (DF)	3	13	172,3	113,8	33,9%

Following the previous consideration, the modification in the system geometry did not provide any improvement of the efficiency. The medium varia instead, the strength of the ion flux is lowered, the desalination treatment is hindered, and so the setup discarded.

3.2. VICENZA STONE DESALINATION

The following section focuses instead on carbonate stone samples desalination named “LGL” and “2” which were put respectively into the electrochemical setup and diffusion setup.

Table 14 Electric values for sample LGL treatment.

V1-2 [2V]	V2-3 [16V]		V3-4 [1V]		
	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
Time (h)					
0,000	0,063	0,126	0,150	2,400	1,800
0,100	0,070	0,142	0,167	2,672	1,720
0,150	0,072	0,144	0,166	2,656	1,710
0,200	0,072	0,144	0,157	2,510	1,700
0,250	0,072	0,144	0,156	2,480	1,690
0,280	0,072	0,144	0,155	2,470	1,690
0,300	0,072	0,144	0,154	2,460	1,690
0,330	0,071	0,142	0,151	2,460	1,680
0,390	0,070	0,140	0,147	2,352	1,670
0,400	0,070	0,140	0,146	2,336	1,670
0,410	0,070	0,140	0,144	2,304	1,660
0,420	0,069	0,138	0,141	2,256	1,660
0,430	0,068	0,136	0,139	2,224	1,650
0,440	0,068	0,136	0,137	2,192	1,650
0,460	0,067	0,134	0,135	2,144	1,640
0,480	0,066	0,132	0,130	2,080	1,640
0,500	0,064	0,128	0,124	1,968	1,630
0,560	0,063	0,126	0,120	1,920	1,610
0,700	0,061	0,122	0,117	1,872	1,600
0,750	0,061	0,122	0,144	1,829	1,590
0,800	0,059	0,118	0,109	1,744	1,580
0,900	0,057	0,114	0,104	1,664	1,570
0,950	0,056	0,112	0,101	1,616	1,560
1,000	0,051	0,102	0,090	1,440	1,590
1,200	0,006	0,012	0,071	1,000	1,510
1,300	0,005	0,010	0,069	1,000	1,500
1,500	0,005	0,010	0,069	1,000	1,500
1,700	0,005	0,010	0,067	1,000	1,500
2,000	0,005	0,010	0,066	1,000	1,490
2,100	0,005	0,010	0,064	1,000	1,480
2,500	0,004	0,008	0,063	1,000	1,480

2,600	0,000	0,000	0,051	1,000	1,470
2,800	0,006	0,012	0,012	0,192	1,240
3,000	0,006	0,012	0,011	0,176	1,240

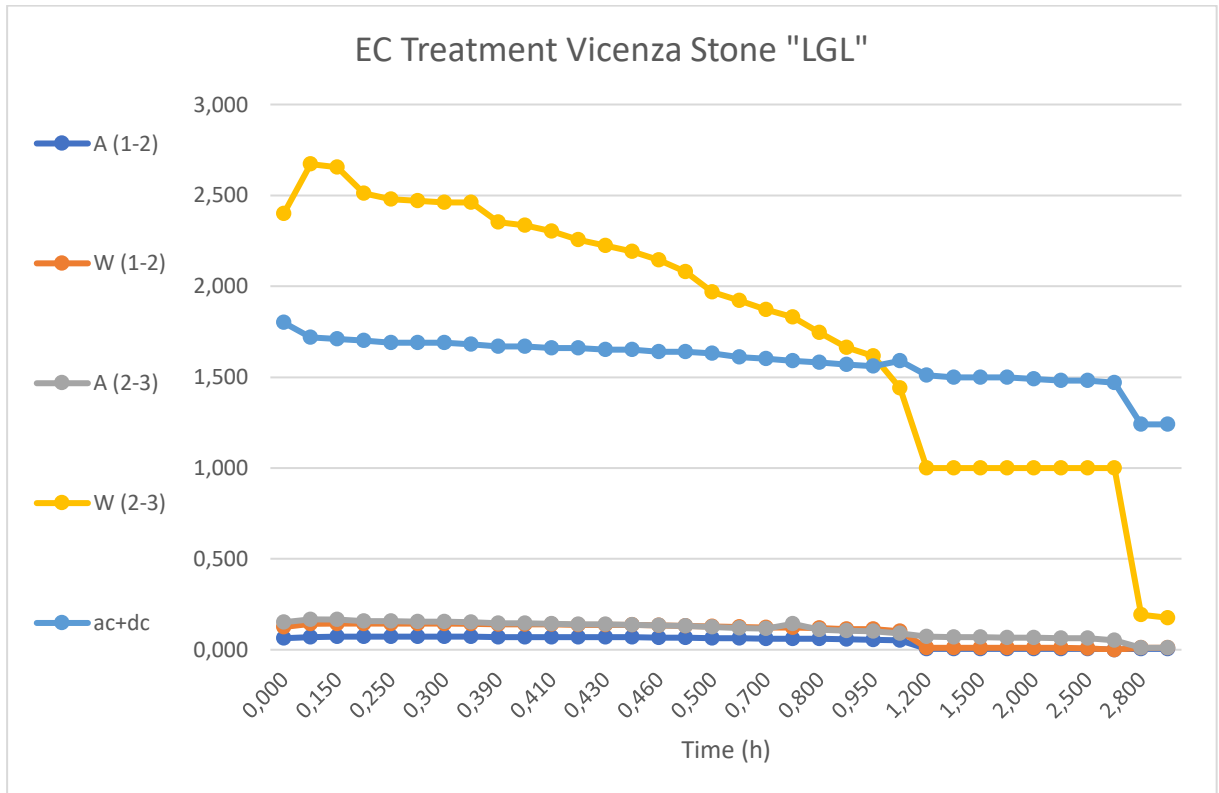


Figure 25 Progression curve for sample LGL treatment.

The behavior of the electrical curves values (fig.25) is slightly different from the ones observed during the treatment of the bricks, both decrease by time passing, until the system reaches stop but with different progression, probably due to the difference in the material composition. The following tab reports the conductivity measurements before and after the desalination treatment.

Table 15 Conductivity values variation for sample "LGL,2"

TREATMENT	SALT CYCLES	SAMPLE	COND. BEFORE ($\mu\text{S}/\text{cm}$)	COND. AFTER ($\mu\text{S}/\text{cm}$)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	"LGL"	208	50	75,9%
DIFFUSION SYSTEM (DF)	3	"2"	157	51,1	67,4%

A good reduction of saline content was achieved: a 75,9% conductivity reduction was obtained from the EC treatment in comparison with the 67,4% from the DF treatment.

Another experiment was run using another pair of Vicenza stone samples. “NG5” was put inside the Diffusion system, while “VG4” inside the EC setup.

Table 16 Electric values for sample VG4 treatment.

V1-2 [2V]		V2-3 [16V]		V3-4 [1V]	
Time (h)	A 1-2	W 1-2	A 2-3	W 2-3	ac+dc
0,000	0,016	0,032	0,073	1,152	1,950
0,010	0,017	0,034	0,071	1,136	1,930
0,020	0,017	0,034	0,070	1,120	1,930
0,040	0,018	0,036	0,067	1,072	1,870
0,050	0,018	0,036	0,065	1,040	1,850
0,060	0,018	0,036	0,063	1,008	1,830
0,070	0,019	0,038	0,061	0,976	1,810
0,080	0,019	0,038	0,059	0,944	1,780
0,090	0,019	0,038	0,057	0,972	1,740
0,110	0,019	0,038	0,055	0,880	1,730
0,120	0,019	0,038	0,054	0,864	1,700
0,160	0,017	0,034	0,052	0,832	1,660
0,200	0,017	0,034	0,051	0,816	1,640
0,220	0,017	0,034	0,044	0,784	1,600
0,290	0,017	0,034	0,047	0,752	1,560
0,350	0,016	0,032	0,045	0,720	1,550
0,410	0,015	0,030	0,044	0,704	1,520
0,490	0,014	0,028	0,041	0,656	1,500
0,520	0,014	0,028	0,040	0,650	1,490
0,580	0,014	0,028	0,039	0,624	1,480
0,620	0,014	0,028	0,038	0,608	1,470
0,740	0,013	0,026	0,037	0,592	1,460
0,820	0,012	0,024	0,034	0,544	1,430
0,950	0,012	0,024	0,032	0,521	1,430
1,000	0,012	0,024	0,031	0,496	1,400
1,050	0,011	0,022	0,029	0,464	1,390
1,080	0,010	0,020	0,027	0,432	1,390
1,120	0,009	0,018	0,024	0,384	1,370
1,190	0,009	0,018	0,022	0,352	1,360

1,210	0,008	0,016	0,021	0,336	1,350
1,230	0,008	0,016	0,019	0,304	1,340
1,300	0,007	0,014	0,018	0,288	1,320
1,500	0,007	0,014	0,016	0,256	1,310
1,800	0,007	0,014	0,014	0,224	1,290
1,900	0,005	0,010	0,010	0,160	1,240
2,120	0,004	0,008	0,009	0,144	1,230
2,500	0,004	0,008	0,008	0,128	1,220
3,140	0,004	0,008	0,007	0,112	1,200
3,150	0,000	0,000	0,007	0,112	1,150

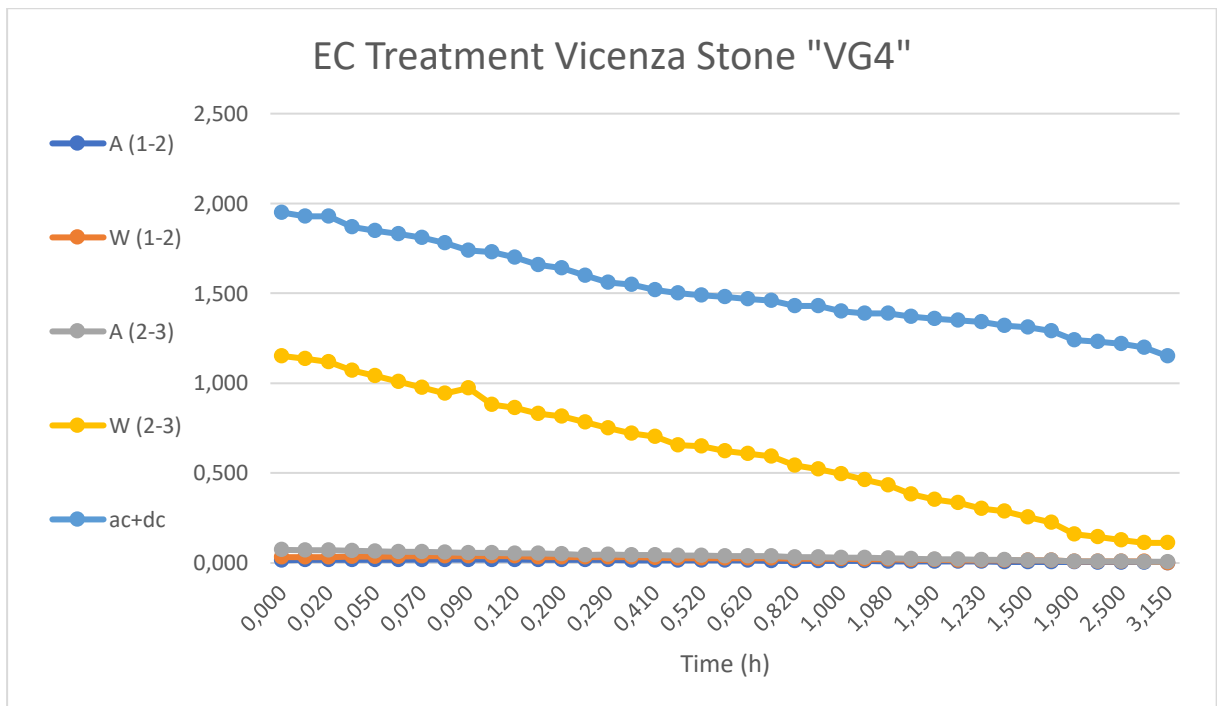


Figure 26 Progression curve for sample VG4 treatment.

As the previous experiment with the Vicenza stone proved, the conductivity reduction of samples that underwent EC system is slightly greater than the ones under DF treatment (tab.16, fig.26). As the below table shows (tab.17), the 62,5% conductivity percentage reduction is greater than the other.

Table 17 Conductivity values variation for sample "VG4, NG5".

TREATMENT	SALT CYCLES	SAMPLE	COND. BEFORE (μS/cm)	COND. AFTER (μS/cm)	Δ CONDUCTIVITY%
ELECTROCHEMICAL SYSTEM (EC)	3	"VG4"	223	83,8	62,5%
DIFFUSION SYSTEM (DF)	3	"NG5"	114	79,9	29,9%

The experience provided useful data regarding the desalination treatment problematics and about the instrumentation needed for the treatments. Starting from the development of the setup, the application of this system to Cultural Heritage samples different from tiles or bricks, or generally small sized samples it's rather difficult, due to the geometry of the electrodes and the poultice system. Complex shaped objects or massive sized specimens (columns, wall portion...) could represent a major limit for this technique. While the implementation of magnesium citrate resulted in an optimal solution against the acidification problem. The modifications to the DAC system adopted during this thesis allowed the production of a simple and replicable method, using multiple layers made by sepiolite and cellulose pulp mixed along with magnesium citrate. The desalination efficiency of this technique has to be seen as purely qualitative due to the lack of efficient methods that determine the exact quantity of salt ions inside a sample without requiring an invasive sampling.

4. CONCLUSIONS

This thesis focused on the study and development of an electrochemical system which could be applied for the desalination of porous materials belonging to Cultural and Architectural Heritage. The electrode-based system was built on previous cases of study by Feijoo et al., concerning a double anode and cathode system (DAC) that induces through a potential difference an ion flux capable of removing salt ions from within the porous sample. Through the implementation of sepiolite/cellulose poultices, the salt ions are extracted and stored until the end of the desalination treatment. As the first experiments have shown, the acidification was a critical point that needed to be overcome in order to progress with the research. The implementation of a buffer solution made by magnesium citrate at pH.7 allowed to maintain stable pH in the system and increase the duration of the treatment. Before and after each treatment, the conductivity measurements for the artificially salted specimens were confronted with in order to determine the effectiveness of the electrochemical method. The variation of salt content was slightly greater in samples that underwent electrochemical desalination rather than the traditional method, so at the current state, the new electrode-based system is only slightly more efficient than traditional methods. Another issue that has been observed, is the lack of methods capable of evaluating the actual efficiency of the treatment, at the moment there is no way for determining the actual content of salt without sampling the specimen directly. During the thesis, the evaluation of the method has been done by measuring the conductivity of the soluble salts, obtained by drilling the sample before and after the treatment.

This electrode-based technique was applied only to specimens artificially salted with NaCl, so mixtures of salts have not been studied yet. Being a relatively young method for desalination of

Cultural and Architectural Heritage, it leaves room for further improvements, like the implementation of an electrode geometry which would allow the desalination of porous stone material by the use of electrodes on only one side of the sample or the development of a conductive grid as a substitute for electrodes, which could be adapted to complex formed specimens.