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Department of Civil and Environmental Engineering
University of Strathclyde

Development of a monitoring method for electro-desalination on Clashach sandstone

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HISTORIC ENVIRONMENT SCOTLAND
ÀRAINNEACHD EACHDRAIDHEIL ALBA

Dedication

To complete a PhD you need to be thorough, meticulous and patient. I have never been patient. I am, however, stubborn as hell and sometimes that can suffice as a substitute.

Declaration

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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Abstract

A non-invasive monitoring method has been developed for electro-desalination (ED) of sandstone. Salts are one of the main culprits in deterioration of cultural heritage, and ED has been proven an effective treatment. However, until now there has not been an accurate non-invasive method to monitor treatment progress. This study investigates the use of impedance to estimate the salt content within a stone sample during desalination treatment. The salt used for the experimental setup have been $NaCl$ due to its commonality in the environment. The stone samples have mainly been Clashach sandstone due to its pure mineralogy and uniform pore size that limits variations during experiments. The experiments trialled a four-point electrode setup and varying boundary conditions. The sensitivity of impedance measurements in relation to inherent variability within samples, porosity, moisture content and salt was investigated. The results showed that neither an individual sample's porosity or composition was directly correlated to impedance. Also, as long as there was more than 20% moisture content within the samples, impedance measurements were not affected. Salt however, clearly impacted impedance values, even at small concentrations. As salt was removed during ED treatment, impedance increased, showing a strong correlation with measured salt values from later destructive testing. The resulting curve of X against Y was robust for all tests. The experiments confirmed that ED is a much more effective method in removing salt compared to poulticing, as well as illuminating three phases of desalination: an initial, high removal rate phase, a constant removal phase and a final increasing phase. This concept needs further investigated and developed. Based on the findings in this study, impedance measurements can be used as a non-invasive monitoring and evaluation method for desalination though ED treatments. Future studies are required to develop a workflow for application in the field.

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1 Introduction

1.1 Thesis rationale

1.1.1 The problem

The latest IPCC report [2021] states that the climate is currently changing at an accelerating pace compared to the past 10,000 years. The global average surface temperature is increasing, and precipitation events are becoming more intense. With the ice caps melting there is also more water available in the atmosphere. With increased water availability, salts will be able to move further into stone structures, potentially creating problems deeper into the matrix. With warmer weather, the solubility of salts will increase and can then gather in higher concentrations within a solution. With more salts further into stone, crystallisation of salt is a significant issue that will lead to faster and more severe salt damage in historical structures. Effective and preferably non-destructive methods to prevent loss of cultural heritage will be needed.

Salt damage is one of the main contributors to the loss and damage of stone heritage objects and buildings. Salt is omnipresent in the environment and enters porous structures while in solution as rain, groundwater and aerosols. When the solution in the pores evaporates, the residual solution becomes super saturated and crystallisation of the salts takes place. This exerts pressure that breaks the stone apart from the inside. This can lead to loss of surfaces or complete decomposition of an object. In 2018, a total of £1.3bn was estimated to have been spent on maintenance and repairs on historic environment sites in Scotland alone [HES, 2019].

The current techniques that are widely used for removing salt from heritage objects are immersion and poulticing. Immersion consists of an object being immersed in water. The salt in the object will then migrate out of the pores on the basis of diffusion. The result is a salt reduction, as the diffusion process dictates that movement of salt will stop once the concentrations are equal in the liquid outside and inside the object. This method requires that objects are of a movable size and are not sensitive to being handled, so cannot be used on highly damaged, fragile stone or on masonry. Poulticing consists of poultices based on clay, sand or paper pulp being applied to the object of interest. By applying a poultice with smaller pores than the structure that contains salt, capillary forces drive the salts from the bigger pores to the smaller pores in the poultice. This method requires that the object is wet enough to connect the poultice and the object of interest, that the surface is stable and that the pore structure has been properly analysed before treatment. If the analysis is wrong, salts could be pushed further into the structure, or migrate to other parts of the pore network. Neither method achieves 100% desalination and both are based on passive mechanisms for the salt to exit the structures and are as such time-consuming treatments.

Electro-desalination (ED) is a remedial treatment that uses electro-migration to force salt ions out of a structure, by applying an electrical current to the object of interest. Because of the active mechanism this treatment can achieve 100% removal of salts and is much faster than the aforementioned treatments. It also has the advantage that it can be used in-situ, negating the requirement of handling and moving potentially sensitive and vulnerable objects. It can be used on a range of porous materials, including sandstone and granite. It requires the presence of water, however unlike other alternative treatments, such as immersion, the object does not need to be saturated. To prevent damage from acidification a pH neutralising agent is required at the anode. Following these precautions, no other damage has been documented [e.g. Ottosen, 2016; Skibsted, 2013]. What is still unknown about this method is how to measure progress of the treatment and to determine when treatment has been successfully treated without using destructive techniques.

Developing a non-invasive monitoring and analysis tool for salt concentration levels would greatly contribute to our understanding of the longer-term side effects of this technique on future material performance. Because samples will not have to be destroyed to evaluate the results of the treatment it opens up possibilities for new ways of determining eventual changes in material behaviour. Potentially it could also provide a tool for conservators to investigate salt content in-situ which could be used as a method to analyse the efficacy of other conservation and salt poulticing treatments, as well as providing an early-warning system for dangerous levels of salt build-up.

Statement of the problem
ED has been proven a more effective salt removal treatment than the current methods. In order to apply it on heritage objects there can be no long-term side effects. To investigate this, a non-invasive monitoring tool needs to be developed.

1.1.2 Thesis aim

The aim of the thesis concerns the development of a non-destructive monitoring tool for desalination treatments in general and ED in particular. This aim can be divided into three objectives which will be addressed in individual chapters.

1. Research the possibility of using impedance measurements as a non-invasive monitoring tool for ED treatment, Chapter 5.
2. Develop a methodology to more accurately measure the impedance of a stone sample being treated with ED, Chapter 6.
3. Investigate if impedance can be used for monitoring the salt movements within a stone sample, Chapter 7.

1.2 Structure of thesis

Following the introduction, Chapter 2 contains relevant theory concerning conservation, ED and monitoring techniques. Chapter 3 describes the techniques used during the lab tests, how to apply ED to stone and how impedance is measured. Chapter 4 provides the material properties of the samples and salts used in the study. These chapters provide the foundations for the investigations of the thesis aim.

Chapter 5 describes method developments done in this study. An electrode set-up for ED treatments that will also enable impedance measurements is presented, together with investigations into boundary conditions for the ED treatment.

The investigation into suitability of impedance as a monitoring tool for salt and moisture movement in stone is presented in Chapter 6, with several variables being measured. Chapter 7 demonstrates the set-up, execution and results of a trial experiment monitoring the ED treatment using impedance.

The thesis is completed by a discussion in Chapter 8 and conclusions in Chapter 9. The discussion breaks down important findings from experiments, postulates how to move the technique developed here forward and recommends future studies. The highlights from the thesis are summarised in the conclusions.

2 Literature review

Electro-desalination (ED) is a stone conservation technique for porous building materials. This chapter presents the relevant information and research on stone conservation (Section 2.1), and the Electro-desalination (ED) method (Section 2.1.4) and what can be done to move the treatment method forward - monitoring methods (Section 2.3).

2.1 Stone conservation

Deterioration of stone can be described as a change in material properties over time. This is a naturally occurring process which is a result of interactions between stone and its surrounding environment. As the surrounding environment is also changing over time, stone conservation requires both understanding of deterioration processes and a dynamic approach to interventions [Viles, 2013]. In this thesis 'stone' is referring to cut pieces of a material and 'rock' is referring to in-situ material in the ground. The focus will be on sandstone but the treatments and problems discussed are also applicable to other types of porous building materials.

To understand how to remove salt most effectively it is necessary to understand how stone is affected by salt weathering, how moisture moves within porous structures, and current conservation practices, specifically desalination treatments.

2.1.1 Flow and drying of porous rock

Moisture transport and drying provides the basis for both salt weathering and several conservation practices (i.e. poulticing). The process of drying is highly relevant for Electro-desalination (ED) treatments as well as electrical measurements which will be covered later in this thesis. This section contains basic information on sandstone as a material as well as basic fluid flow theory before drying principles are presented.

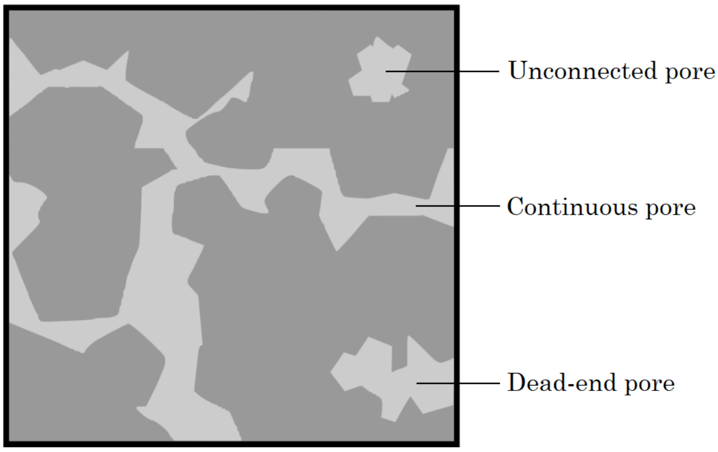


Figure 2.1: *Pore type denomination within pore structure, after Lehmann [2018].*

Sandstone is a versatile building stone that is widely used in Scotland and throughout the world. It is a common rock type that can be easily carved compared to other types of stone. It is largely made up of particles of silicates such as quartz or feldspar that have weathered from existing rocks into sand sized grains, hence the name. These sand grains are then transported by water or wind to depositional environments such as valleys, flood plains or the sea. Here the grains accumulate and undergo lithification: over time and under pressure the sand grains consolidate, the porosity is reduced, and connate fluids are expelled. The resulting pore structure will contain several types of pores; continuous, unconnected, and dead-end pores, illustrated in Figure 2.1. The pore structure enables moisture and salts to be transported within the pores.

For moisture transport within a porous media, Darcys law can be used (Equation 1) to calculate the flow through a particular medium.

$$Q = \frac{Ak\Delta P}{\mu \Delta x} \tag{1}$$

Q - Volumetric fluid flow
A - Area of medium
k - Permeability of medium
μ - Viscosity of fluid
ΔP - Applied pressure difference
Δx - Thickness of medium

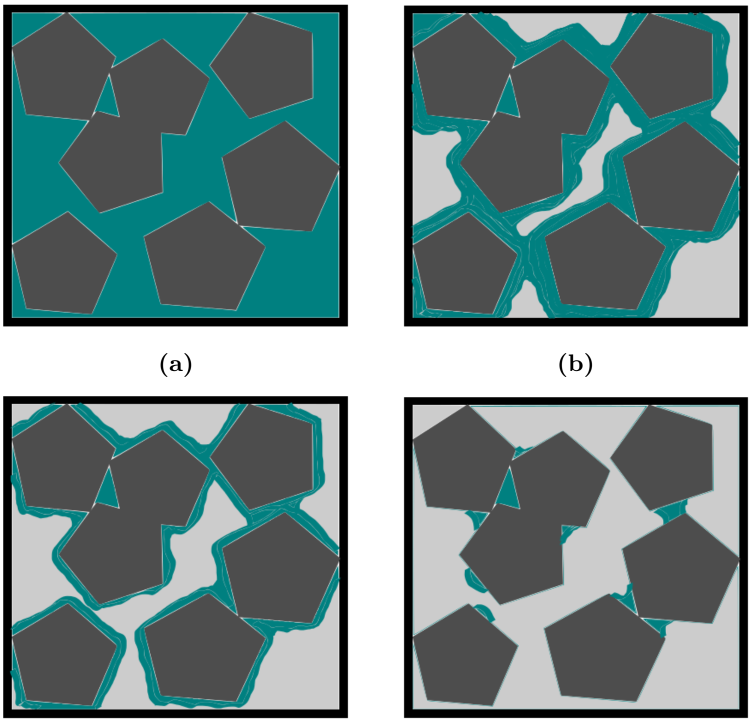
The permeability is a description of the material's ability to transmit fluids and is dependent on the porosity, but how well connected the pores are. Viscosity is a property of liquid that describes its resistance to flow.

The pressure difference, together with the cross sectional area and permeability of the sample is divided by the fluid's viscosity and the sample's thickness (distance that the pressure drop is measured across). The resulting fluid flow is the amount of liquid that is transported through the pores given a certain pressure gradient.

When drying of a porous material is first initiated, the liquid meniscus retreats from the surface into the pores. There is however still a liquid film on the pore walls that enables fluid flow towards the surface. As the drying continues into the second stage, the film thickness decreases until the surface tension of the water is overcome and the liquid film layer breaks apart [Scherer, 1990]. This is illustrated in Figure 2.2.

Drying can be divided into two stages, Stage I: the constant drying rate and Stage II: the falling drying rate. The stages are defined by what is controlling the drying process. Throughout drying, capillary flow supplies the surface with water for evaporation. During Stage I, the drying rate is dependent on external conditions and not on any capillary processes within the material. Once water cannot be supplied to the surface fast enough to satisfy the evaporation process, Stage II drying takes over. The drying process is now dependent on the unsaturated flow within the pore structure [Hall and Hoff, 2009].

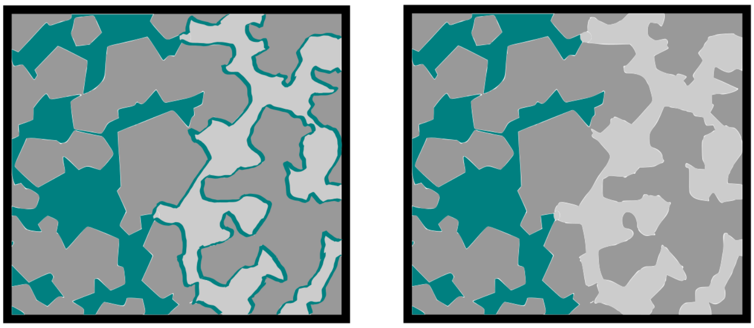
Figure 2.3a illustrates the water filled pores and a drying surface (right) though a liquid film, supplying the surface with more water. Once the connection between film and water filled pores is broken, and stage II drying is taking place, a drying front is developed. Figure 2.3b illustrates a drying front, where part of the sample is filled with air and part is saturated with water. This phenomenon can impede both water transportation and electrical conductivity.



(a) **(b)**

(c) **(d)**

Figure 2.2: *Illustration of how drying occurs in porous media. (a) 100% saturated pore structure (b) Drying, air replacing water in larger pores, a film connected through the pores (c) Further drying, film thickness reducing. (d) Once surface tension is broken, the water is disconnected through the sample.*



(a) **(b)**

Figure 2.3: *(a) Drying stage I. Water is supplied towards the drying surface (right) though a liquid film connected to the water filled pores deeper within the pore structure. (b) A drying front of air filled pores, the liquid film between surface and water filled pores has been disconnected and disappeared.*

2.1.2 Salt weathering

There are many agents behind stone decay, for example air pollution, salts, biodeterioration and physical stresses [Doehne and Price, 2010]. This thesis will focus on salt damage, as salt damage together with stone cleaning and repairs using incompatible materials is one of the main issues of decay for the built environment. The two latter problems are entirely dependent on human intervention and can be avoided by not applying these treatments. Salt damage, however, is a natural part of the life cycle of rock [HES, 2005]. Deterioration from salt leads to the integrity of the material decreasing, where it becomes more sensitive to further salt damage as well as other forms of decay. This leads to the irretrievable loss of valuable cultural heritage.

Salt damage is a naturally occurring phenomenon that accelerates stone deterioration. Most commonly, the salts enter the material by capillary rise from the ground water or through infiltration of rainwater. The salts have many origins, including sea spray, soil, de-icing salts and air pollution. Within the pores, the movement of salt is dictated by the temperature and relative humidity of the surroundings, as well as the presence of other salts. It is rare that damage occurs from the presence of one salt only [Charola, 2000].

Salts are ionic compounds comprised of positively charged cations (i.e. Na^{+}, Ca^{2+}) and negatively charged anions (i.e. Cl^{-}, SO_4^{2-}). When in solution, they can be dissolved into separate ions and move into or around within porous building materials such as sandstone. When the relative humidity (RH) of the ionic solution is higher than the ambient RH, salt can precipitate in the matrix or on the surface of the stone [Goudie and Viles, 1997]. The crystallisation of salts has long been established to damage building materials, but there is some disagreement on the actual mechanisms behind the salt damage [Charola, 2000].

The main theory is that salt deterioration is a result of salt crystallisation. This happens when an ionic solution is super-saturated, either though evaporation of liquid or temperature changes. Once the conditions are in place, a nucleus of solid salt is formed, and it grows within the pore network. This exerts pressure on the solid material between pore spaces. When enough pores are under pressure that the tensile strength of the stone is surpassed, the material breaks apart [Ruedrich and Siegesmund, 2006].

Damage that can be expected from salt deterioration includes: scaling (part of the surface opening and potentially falling off in "scales"); cracking, granular disintegration when minerals separate into grains; delamination as layers of materials separate, opening the structure or falling off in sheaths [Doehne, 2002]. The variability in deterioration patterns depends on the materials and salt combinations [Charola, 2000].

Salt weathering is a global challenge, leading to irreparable damage to heritage objects, as well as modern infrastructure [Goudie and Viles, 1997]. It is a process escalated through cycles of wetting and drying [McCabe et al., 2013]. Global warming is currently impacting climate changes around the world. The projection for the current century includes an increase of the global average temperature, higher minimum and maximum temperatures, increased and intensified precipitation, with more varied year to year variations [IPCC, 2021]. The increase in temperature and water will lead to more frequent wetting and drying cycles, which in turn will increase damage to stone from salt. Therefore, finding a method to slow deterioration from salt could be crucial, to potentially save monuments that otherwise would be lost in the years to come.

2.1.3 Conservation practices

Stone conservation can be divided into preventative conservation, where any actions taken address the environment around an object using minimal intervention, and active conservation, where a problem is dealt with within the structure. Within the sphere of conservation ethics, there is also the discussion if any action should be taken at all [Doehne and Price, 2010].

Preventative Conservation
When possible, preventative conservation can address the direct air around heritage objects, with control of RH and temperature. This is possible in museums, but not so much for unmovable and larger projects. In this case indirect actions can prevent water from gathering on or around the stone. Water can be prevented from entering the area using a rain shelter, or excess water can be lead away using a drainage system. Another large part of this type of conservation can be collectively gathered under the term management. It contains legislation, disaster planning and control of pollution, traffic, or groundwater. Finally, preventative conservation also addresses visitor management, such as establishing paths, fences, or signs to avoid human interactions with sensitive objects or sites [Doehne and Price, 2010].

Active Conservation
Any action upon the stone itself is considered active conservation. The main activities that heritage objects undergo fall under one of the following categories: cleaning, desalination, consolidation, or surface coatings [Doehne and Price, 2010]. Desalination will be addressed more in detail later on in this section (Section 2.1.4), but the other treatments are briefly presented here.

Cleaning serves the purpose of removing dirt to make a better assessment of what conservation may be necessary or removing harmful materials from the objects surface. However, cleaning is often done from an aesthetic point of view. The act of cleaning buildings is argued by some to be the opposite of conservation, as it is irreversible, and the evidence of history is removed [Doehne and Price, 2010].

Consolidation is the act of inserting a substance into the decaying stone that binds it together with the solid stone underneath, preventing deterioration to continue. The active substance needs to have the same material properties as the stone once it is in place there, and the most well-established use is to use lime wash on limestone, to consolidate the calcium carbonate structure within the stone. There are more modern types of consolidants as well, but the research for the optimal addition is still ongoing [Doehne and Price, 2010].

Surface coatings refers to application of treatments by water repellents, preventions against graffiti and salt inhibitors, amongst others, onto an objects surface. All these treatments need to be maintained to not accelerate the deterioration that it was applied to avoid [Doehne and Price, 2010].

Conservation ethics

Historic Environment Scotland describes the purpose of conservation as the perpetuation of culturally significant objects and sites. The significance and history of each site therefore needs to be considered before any action is taken. The context and authenticity of each object must be considered, and the original design intent should be respected. Potential future climate changes have to be addressed, and conservation has to be considered above other demands of a historic site. The appropriate knowledge, skill and materials should be ensured, and any interventions should be recorded and archived to assist future generations of conservators [HES, 2015].

The nature of the deterioration can be described as either chronic or acute, the treatment of these might be severely different. Smith and Přikryl [2007] also state the importance of treating causes rather than symptoms of damage. As stone decay is a natural process, they argue that instead of prevention, conservation should allow monuments to ”grow old gracefully”.

Treating salt damage

The approach to treating salt damage will depend on the sources and pathways of the salt. Some salts are part of the stone structure itself, as is the case of $CaCO_3$ in Limestone. Other sources are the accumulation of salts from the historic usage of the site, such as table salt storage or a stable that housed manure, which contains sulphates and nitrates. Modern sources also include the use of pesticides or road salt in the vicinity of the structure. The natural sources also include rising damp from soil, rain, and sea spray [Charola and Bl auer, 2015].

The key to any treatment is an accurate diagnosis of the problem, as administering the wrong type of treatment might not only not improve the situation but also make it worse. Whenever possible, the best intervention for salt damage is leading away any excess water, preventing accumulation of new salts. When the damage is already done or comes from within the stone or historic use, a desalination treatment can be an option. If the source of the salt cannot be removed or disrupted, and is continuous, one strategy can be to control the surrounding environment of the object to prevent crystallisation cycles [Viles, 2012].

2.1.4 Desalination treatments

Van Hees et al. [2009] researched desalination for monumental buildings, focusing on two methods for salt reduction treatments, immersion, and poulticing.

Immersion

For smaller, movable objects that are not sensitive to water, immersion is the established method to remove salts. The object is submersed in a bath of water, and the salt is transported out of the object through diffusion. When there is a concentration gradient of ions, diffusion is the process of ions at the high concentration area moving towards the lower concentration area until an equilibrium is reached. The bath water gets replaced until salt is no longer extracted. As effective as this treatment is, it is not applicable to a variety of objects, including ones with sensitive surfaces, ones that contains water soluble compounds or objects that are non-movable [van Hees et al., 2009].

Poulticing

For larger and non-movable objects, poulticing is the most common salt reduction treatment. The method varies but generally consists of two parts. First, a wetting phase in which water is transported from an applied poultice into the stone where the salt will be dissolved. Second, an extraction phase where the dissolved ions migrate into the poultice. The extraction takes place through two different processes: diffusion and advection. Diffusion causes the equalling out of concentration gradients, through movement of ions along those concentration gradients. Advection takes place by capillary water flow, where the salt follows the flow of water, in this case through the process of drying (Section 2.1.1). As advection is a faster process than diffusion, it is desirable to optimise the poulticing treatment to ensure advection is the dominant transport mechanism [Pel, Sawdy and Voronina, 2010].

Relying on diffusion as a poulticing technique, any poultice will work independently of pore size but is very slow (weeks, months). Advection poulticing is faster (days) but is pore-size dependent, and requires an adaptation of the poultice for each treatment object. Also, when advection is the main transportation mechanism, there will be back diffusion. Back diffusion is when salt diffuse back into the area from which it was just removed as a result of a concentration gradient. For both methods, moisture must be added, which can lead to water related deterioration. In practice, it is not achievable to attain 100% salt removal as ever diminishing concentration gradients effectively make the process go on for ever [Pel, Sawdy and Voronina, 2010].

Challenges

For both immersion and poulticing, the treatment is more effective towards the surface, and can present challenges such as salt migration to new areas of the stone and precipitation of salt in the pores (sub-fluorescence) [van Hees et al., 2009]. The efficiency of salt removal is measured by the amount of salt extracted. However, it is arguably better to focus on the distribution and behaviours of any residual salts, to prevent undesirable effects from the treatments [Sawdy, Heritage and Pel, 2008].

Electro-desalination (ED)

Electro-desalination (ED) is a desalination treatment in which poultices are placed on the surface of an object, and electrodes are placed externally on the poultices. An electrical direct current is applied across two electrode/poultices, driving charged ions to the electrode with the opposite charge. The ions gather in the poultices by each electrode and once the treatment is complete, the poultices containing the salt ions are removed [Ottosen and Hansen, 2016]. The method will be described in detail in Section 2.2.

The addition of a driving force (electricity) for the ions improves the efficiency of salt removal compared to traditional poultice treatments and can be applied without calibrating each poultice for individual projects. However, it adds the challenge of pH changes within the poultice and the adjacent stone, which may affect the material properties of the stone treated [Ottosen and Rörig-Dalgaard, 2007].

The main improvement between poulticing and ED is the speed and control of the ion migration, together with a minimisation of residual salt within the treated objects [Ottosen, 2016].

2.2 Electro-desalination (ED)

Electro-desalination is a remediation technique used on porous building materials, in which dissolved salt ions within the treated object are transported to the electrodes placed on its surface. This section describes the electrochemistry, application, previous studies, and current challenges of the method.

2.2.1 Electrochemical principle of ED

ED treatments use the principles of electrolysis and electromigration in order to separate and remove salts from stone. These and other terms of electrochemistry are described further below.

- Electrolysis: Application of direct current (DC) through an electrolyte to cause chemical reactions at electrodes.
- Electromigration: The movement of ions in solution because of an applied electric field.
- Electroosmosis: Movement of water within a capillary generated by an electric field.

When applied to porous inert materials such as sandstone, all these effects will take place within the pore space of the stone. From herein, the material to be treated will be referred to as sandstone, but the principle is effective on many other materials [e.g. brick and tiles: Ottosen and Rörig-Dalgaard, 2009; Ottosen, Ferreira and Christensen, 2010; limestone and granite: Feijoo, Ottosen and Pozo-Antonio, 2015; Herinckx et al., 2011].

Electrolysis
Electrolysis is the process of applying DC over a conductive solution (electrolyte) in order to create chemical reactions at the electrodes [Dziubakiewicz and Busewski, 2013]. During electrolysis, both salt and water ions will separate. The salt separation processes are presented in the following equations, for the separation (2), the reduction process at the cathode (3) and the oxidisation process at the anode (4).

Separation process:

$$NaCl(s) \rightarrow Na^{+}(l) + Cl^{-}(l) \tag{2}$$

Cathode process:

$$2Na^+ + 2e^- \rightarrow 2Na(s) \tag{3}$$

Anode process:

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \tag{4}$$

The water of the ionic solution will also separate, into hydrogen at the cathode (5) and oxygen at the anode (6)(7) [Ottosen and Rörig-Dalgaard, 2009].

Cathode process:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \tag{5}$$

Anode processes:

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2(g) + 2e^- \tag{6}$$

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2(g) + 2e^- \tag{7}$$

Because of these electrokinetic processes (5-7), the pH will change around the electrodes. The area around the anode will become acidic as the concentration of H^+ increases. The area around the cathode will become more alkaline as the OH^- concentration increases.

Electromigration

Electromigration is the movement of salt as a result of an applied electric field. The dissolved salt ions have an electrical charge, and they will migrate towards the opposite charged electrode [Ottosen and Rörig-Dalgaard, 2009], as illustrated in Figure 2.4.

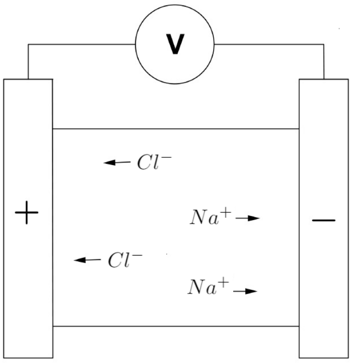


Figure 2.4: *Basic principle of electromigration in an ionic solution. Sodium and chloride ions move towards the electrode that is charged opposite to the ion.*

Several different types of salt have been removed from building materials through ED in the past, e.g. $NaCl$, Na_2SO_4, $NaNO_3$, $Ca(NO_3)_2$ & KCl [Herinckx et al., 2011; Ottosen, Dias-Ferreira and Riberio, 2015; Ottosen and Rörig-Dalgaard, 2007; Ottosen and Rörig-Dalgaard, 2009].

Electroosmosis

Electroosmosis is a transport mechanism for fluid that occurs when electricity is applied across a wet, porous material. The inner surfaces of sandstone pores are negatively charged, which attracts positive ions. These positive ions gather along the surface of the pores, creating a positive electric double layer. When an electric field is applied over the sandstone, the double layer will move towards the cathode, creating electroosmotic flow (EOF) of the fluid within the pore. Figure 2.5 illustrates the gathering of positive ions along the negatively charged pore surface.

Figure 2.5: *Positively charged electrical double layer on the inner surface of a negatively charged capillary, resulting in an electroosmotic flow (EOF) towards the cathode, after Dziubakiewicz and Busewski [2013].*

The electroosmotic flow is influenced by the pH of the solution. At lower pH, the flow is low and at high pH the flow is faster [Thormann, 2018]. It has also been observed that the electroosmotic transport of water for most porous materials is towards the cathode [Ottosen and Rörig-Dalgaard, 2009]. Meanwhile Dziubakiewicz and Busewski [2013] notes that the electroosmotic flow can be strong enough that it forces dissolved ions to join the flow of the fluid, no matter the charge of the ions.

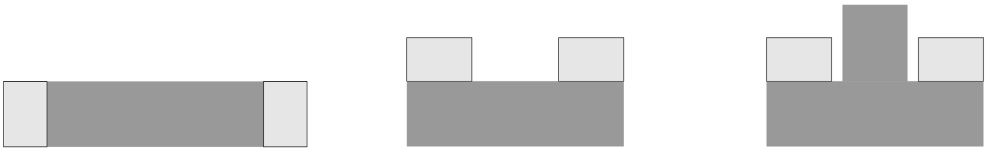
2.2.2 Applying electrical current to stone

Current (I) is the flow rate of electrons, and resistance (R) is the push against the electrical current. The electric potential (V) is the resulting force that needs to be applied to get a specific number of electrons from point A to point B for those specific conditions. If the resistance is constant, an increase in flow rate (current) requires a higher electrical potential, following Ohm's law:

$$V = IR \tag{8}$$

Electrical current will follow the path of least resistance. As the grains in a sandstone are a relatively non-conductive material, the current will move through the pore system of the stone. Therefore, the connectivity of the pore network is a determining factor for a stone's conductivity [Lehmann, 2018].

When administering a current on an object, the connection between electrodes and object is key. In ED this is addressed by using a moist and malleable poulticing clay to connect the electrodes and the stone [Rörig-Dalgaard and Ottosen, 2009]. The clay is usually wrapped in plastic to delay evaporation of water, and depending on the treatment time will be exchanged with new clay periodically [Rörig-Dalgaard, 2013]. Electrodes can be placed opposite each other (Figure 2.6a) or parallel to each other (Figure 2.6b) with successful results [Ottosen, Skibsted and Præstholm, 2014; Norsk and Andersson, 2016]. It has also been pro-ven possible to desalinate objects with protruding parts, without direct contact to the protrusion (Figure 2.6c) [Andersson, 2017a; Feijoo et al., 2017].



(a) **(b)** **(c)**

Figure 2.6: *Electrode placements during ED treatment. a) Opposite b) parallel c) avoiding contact with protrusion*

The results concerning the desalination of protrusions can be a solution to desalination treatments of statues and other decorations without exposing said decorations to further damage from physical interference. For bigger monuments such as buildings, pilot studies have been undertaken. A series of electrodes have then been placed on a wall using clay forms mounted using drilling [Ottosen, Rörig-Dalgaard and Villumsen, 2008; Ottosen, Christensen and Rörig-Dalgaard, 2012]. This is an invasive technique and might not be suitable for all monuments.

2.2.3 Purpose and effect of poultices at electrodes

As described in Section 2.2.2, ED treatments use poultices for connecting electrodes to the stone. The poultices also contribute to the treatment in other ways, which are presented here.

Use of poultice clay

The most common method to apply ED in the lab is illustrated in Figure 2.7. When treating objects in-situ, individual solutions have been developed [Ottosen, Christensen and Rörig-Dalgaard, 2012; Feijoo et al., 2018b]. The stone to be treated is in the middle. Kaolin based poultice clay is attached to the stone on two sides and the electrodes are in turn placed on the outside of the poultice.

The poultice clay ensures a stable electrical connection between electrode and stone through its consistency and moisture content. It also gathers the removed salt, so that once the poultice is removed, so is the salt. The removed poultice can be analysed to investigate the amount of salt removed from the stone. Finally, the poultice can help prevent pH changes in the stone through buffering the chemical reactions taking place at the electrodes.

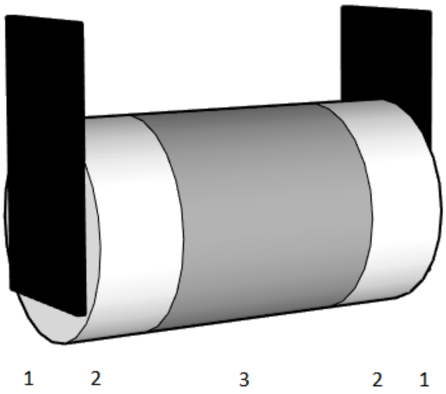


Figure 2.7: *Current concept of electrode set-up. 1) Electrodes; 2) Poultice; 3) Stone.*

pH changes
The ED treatment results in pH changes as described in Section 2.2.1: the area around the anode will become acidic and the area around the cathode will become alkaline. In Herinckx et al. [2011], ED was administered without any pH buffering, resulting in severe deterioration. They state the importance of protecting masonry against acidification and organic compounds from alkalisation.

Desalination can be achieved without preventing the increased concentration of OH^- ions at the cathode [Rörig-Dalgaard, 2013]. However, it has been shown that it can lead to a slower removal process during ED treatment. This is because OH^- has a higher charge transfer than the other ions present [Ottosen and Rörig-Dalgaard, 2009]. Further studies have been done to investigate buffering agents to avoid the alkalisation at the cathode, but no useful solution has been found [Rörig-Dalgaard, 2015].

Some building stone is bonded with, or contains grains of, calcium carbonate. If these stones are treated with ED without a buffer against acidification, they will start to disintegrate [Herinckx et al., 2011]. This is because introduction of H^+ to a system containing $CaCO_3$ leads to the calcium carbonate dissolving to form solitary Ca^{2+} ions together with carbon dioxide and water, as in Equation (9).

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2(g) + H_2O \tag{9}$$

$CaCO_3$
Because of this chemical reaction, $CaCO_3$ is an ideal component to add to the buffering clay to prevent acidification in the stone, as illustrated in Figure 2.8. The first reaction is when hydrogen splits at the anode, releasing electrons, hydrogen ions and oxygen in gas form. The electrodes move toward the electrode, and the oxygen gas tries to escape where it can, or else creates gas bubbles in the clay. The collection of hydrogen ions raises the pH of the area around the anode. The second reaction is when hydrogen ions interact with calcium carbonate

to create bicarbonate, and release calcium ions. The calcium ions have a positive charge and will therefore start to migrate through the clay, then the stone, towards the cathode. The bicarbonate can interact with hydrogen ions from the first reaction to form the third reaction, creation of water and carbon dioxide gas. The carbon dioxide tries to escape or form bubbles like the oxygen gas in the first reaction. The water starts the process over again. This is how $CaCO_3$ neutralises the acid created at the anode.

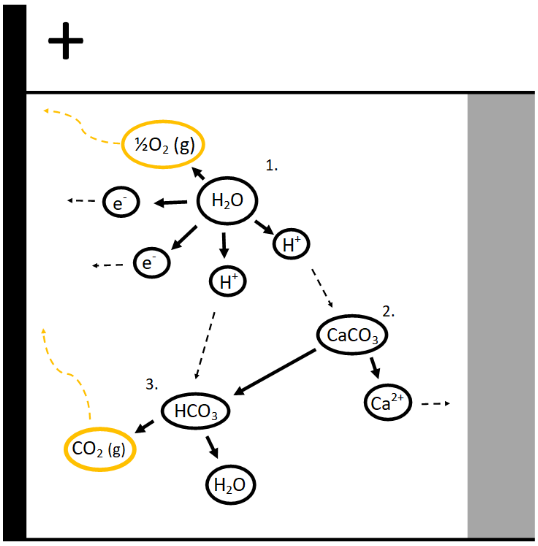


Figure 2.8: *Acidification and buffering processes at the anode: 1.) Water dividing at the anode, resulting in oxygen, loose electrons and hydrogen ions 2.) Hydrogen bonding with calcium carbonate creating bicarbonate and releasing calcium ions 3.) Bicarbonate and hydrogen forming water and carbon dioxide.*

If the positively charged hydrogen ions are not controlled within the clay, they will enter the stone as they are drawn towards the negatively charged cathode. This could impede the desalination of the ions of interest, and it could also lead to precipitation of new calcium-bearing salts, further discussed in Section 2.2.4. This can be prevented by changing the clay poultice, thus removing any solitary calcium ions, and providing fully bonded calcium carbonate [Rörig-Dalgaard, 2015].

Introducing silk paper membranes

A potential problem of using poulticing clay on historical monuments was found by Rörig-Dalgaard [2013]. The kaolin clay left marks on the treated material, which is not acceptable for historical monuments. Feijoo et al. [2017] suggested the use of a silk paper membrane to prevent this.

2.2.4 Challenges for application

The ED method has been tested in lab environments, with limited trials in-situ [Ottosen and Hansen, 2016]. In order for ED to be equivalent or better than existing techniques it must offer cost and/or time reductions, be portable and applicable to both minor monuments and larger stone structures and not damage the stone in short-term (during treatment), or long-term (i.e. change the stone properties so as to be more vulnerable to weathering). The main challenges of applying ED on historical monuments are described here.

Large scale objects

Successful treatment has been made on small scale objects [Ottosen, Skibsted and Præstholm, 2014] and even on protruding objects [Feijoo et al., 2017]. For application on larger objects such as walls, electrode and clay compartments that can be attached to walls by screws with minimal invasion have been conceived [Ottosen, Rörig-Dalgaard and Villumsen, 2008]. This means that the treatment is no longer non-invasive in cases of vertical application. The compartments also fill the function of keeping the poulticing clay moist throughout treatment.

The size of the object is one of the main factors to determine the applied electrical current needed to complete desalination. This could potentially require a potentially harmful level of electrical current, but Ottosen solved this by using pairs of electrodes, minimising the area of each electric field [Ottosen, Christensen and Rörig-Dalgaard, 2012]. This means that larger areas can be treated using less electrical current.

Apart from walls and large structures, there are also smaller monuments which are not movable, but cannot be treated with electrode compartments which are invasive. When treating an object outside, the environment can largely not be controlled. The main issue that has to be considered is the moisture content of the object to be treated.

Without moisture, the salt will not be in solution and as such cannot move. It is therefore essential that the object to be treated has a certain amount of moisture for the treatment to be effective. This amount of necessary moisture has not been investigated. Most studies that are taking place in lab settings are done using complete saturation, which is not applicable in-situ. Still, studies have been done showing successful treatment with moisture content as low as 1.3w% and 1.6w% in sandstone [Matyščák, Ottosen and Rörig-Dalgaard, 2014; Ottosen and Christensen, 2012]. This indicates that objects need to be wet, but not saturated for successful treatment. Whether or not wetting of objects is required before ED treatment will therefore be dependent on the individual situation.

Influence of salt origins

Apart from object size and water content, the ED treatment will also depend on the salt present in the stone, including type, concentration, and combination of salts.

Salt can originate from one or more of the following type of sources;

- within the object, for example if salt water has been used when mixing mortar
- from the surface in the form of liquid or aerosols, for example rain or sea spray
- through capillary rise from the ground

In the first case, the salt within the structure will at some point be approaching zero and as such, no side effects in the form of new salt deposits or patterns are to be expected.

In the second case, when salts enter the structure from the surface, there will be a continuous deposition of salts during and after treatment, unless the source of the salts can be removed for example by installing a shelter to prevent rain from accessing the surface. In order to keep the object salt free, the treatment then has to be repeated. It will have to be considered in each case when ED treatment is appropriate, and if it should be repeated to prevent new salt deposits from accumulating.

The third source of salt is from ground water. In this case it could be conceived that by removing salt from part of the structure, diffusion would act to migrate more salts towards the surface. In some cases, it could be argued that desalination would therefore be a futile endeavour. ED treatment is more ideal in situations where a salt deposit needs to be cleared once, or possibly a few times but over a long period of time. It would not be advisable to use it as a continuous treatment as it would be costly in time for a low reward.

Precipitation of salts

One of the main worries concerning desalination treatments is the precipitation of salts within the pore structure. Salt formation could hamper the desalination effects as it could "clog up" pores, but also, it might create damage in the material from salt crystallisation. As the electrical field will force ions towards one of the electrodes, precipitation of salt already present within the system is only a consideration if there is not sufficient moisture content.

However, as Ca^{2+} ions are released at the anode clay as a result of the pH buffering, it is possible that $Ca(OH)_2$ might precipitate as there is expected to be unbound OH^- migrating from the cathode. This might in turn react with CO_2 from the air to form $CaCO_3$. Neither of these are considered damaging according to Ottosen and Christensen [2012]. Rörig-Dalgaard [2015] suggested it could be positive in the case of limestone, where $CaCO_3$ is part of the original matrix of the stone.

Another salt that might precipitate is $CaSO_4$, if any unbound SO_4^{2+} is present. This is suggested through modelling in Paz et al. [2013]. Skibsted [2013] tried to use XRD to investigate this formation, but the highest possible amount of salt formed was found to be below the XRD detection limit. It was however concluded that eventual salt precipitation did not prevent successful desalination.

Damage detection

Deterioration of ED treated materials has been investigated in the form of porosity [Skibsted, 2013], visual appearance and compressive strength [Ottosen, 2016]. However, other physical alterations such as changes to the pore/grain structure (i.e. pore size distribution, permeability or grain compaction) have not been evaluated. The main reason for this is that most of the techniques for evaluating these properties are destructive (i.e. MIP, XCT, SEM). This means that the same sample cannot be tested for pore structure properties twice. This can be circumvented by using many samples and based on other non-destructive measurements (i.e. porosity) and assuming similarities between them.

As the techniques for evaluating the success of the treatment are also destructive (IC/ICP), the same sample can also not be confirmed to have been both desalinated and deteriorated. To avoid using a large host of samples, it would be desirable to have a non-invasive monitoring technique that can be used to describe both the treatments progression and conclusion without damaging the samples. A precise monitoring technique would also minimise treatment time.

2.3 Monitoring methods

Monitoring remedial treatments is essential to see how the treatment is progressing. Monitoring can define when treatment is complete and by not exceeding the time needed for completion, eventual damage from prolonged treatment can be minimised. While damage has not been demonstrated to occur, treating objects for less time will minimise the risk that undetected damage will affect the long-term lifetime of the stone, and saves money and the time for which a monument is hidden from public view. Until now, there has not been an effective tool developed for monitoring desalination treatment. This study has sought to address this problem.

2.3.1 Current monitoring methods for ED

Rörig-Dalgaard and Ottosen [2009] started with applying a constant current, measuring the resulting potential difference as a monitoring technique. This is due to the relation between potential difference, current and resistance, presented before in Equation 8. At a constant current, the ED treatment will result in an exponentially increasing potential difference, indicating a rising resistance as a result of removal of charged ions in the system [Rörig-Dalgaard, 2013]. The same scientists and others have also been applying a constant potential difference, then monitoring the decreasing current [e.g. Ottosen and Hansen, 2016; Feijoo et al., 2018b]. This method minimises eventual side effects to the treated object in case of prolonged application, as the increase in resistance will result in a reduced current. It will however also reduce the transportation rates of ions over time as this is dependent on the current. Both methods of application are still in use.

Kamran et. al. [2012] used a NMR setup for monitoring the ED treatment of bricks, where they were able to monitor the movements of water and sodium, but not chloride. Combined with the method being expensive and only applicable in a lab setting, this method has not been taken further.

Completion of ED treatments has mainly been determined in two ways: a reduction of current until desalination can no longer take place in the case of applied voltage, or an increase in voltage in the case of applying current. In the latter case the treatments have been considered complete when the voltage increased significantly compared to the initial value or reached the maximal potential of the power supply, in the case of Ottosen and Rörig-Dalgaard [2009], this was 136V. This is because as the sample is desalinated, the voltage increases exponentially.

Both these monitoring methods consider the whole system, including poulticing clays and stone.

The movement of salt within the system is not considered. This means that the resistance measured is not necessarily a measurement of the desalination process but could also be a result of disconnection between poultices and stone or a reduction in the overall water content of the system (e.g. by water leakage or evaporation). A more ideal monitoring method would provide information concerning what is happening within each part of the system during treatment, specifically the stone to be treated.

2.3.2 Possible monitoring improvements

An improved method for monitoring the ED treatment should be able to determine what is going on within the stone that is being treated without the influence of the poultice clays, in a non-invasive manner. This is because the current method of determining the salt content of the treated object, is to destroy it for measurements (Section 3.5), which is not desirable for historical monuments which are sensitive to invasive (damaging) testing and sampling.

Although there already are several non-invasive monitoring techniques available for moisture measurements [Orr, 2021], this is not the case for salt monitoring [Sawdy, Heritage and Pel, 2008].

Recently, Lehmann [2018] has developed a method for moisture monitoring through impedance on porous materials, with the ability to negate the impacts of salts on the measurements. For this study, it is of interest to find out if the opposite is possible, to determine the salt content of an object using impedance.

The reasoning behind using impedance as a salt indicator is that building stones are generally considered to be electrically inert materials, as their composition does not encourage a transfer of current between electrons. Therefore, any conductivity/resistivity/impedance measured on porous materials such as building stones can be related directly to the pore space and its contents [Schön, 2015].

The novelty of monitoring the ED treatment using electrical resistivity/impedance is that the remediation and monitoring methods can be combined.

2.3.3 Electrical impedance

Electrical impedance is a measure of a material's opposition to transmitting electrical current when applying a potential difference (voltage), and similarly for voltage if an electrical current is applied [Lasia, 1999]. Impedance (Z) is represented as an imaginary number:

$$Z = Z_{mod}(cos(\phi) + isin(\phi)) = Z_{mod}e^{i\phi} \tag{10}$$

$Z_{mod}(\omega)$ is the frequency-dependent magnitude of impedance, i is the imaginary unit, and $\phi = arg(Z)$ is the phase angle between real and imaginary components. The real component $Z_{real} = Re(Z)$ represents the electrical resistance of the system, and the imaginary component $Z_{imag} = Im(Z)$ represents the reactance. The reactance is comprised of inductive and capacitive elements [Biondi et al., 2020].

Impedance can be used to detect water and salt movement in porous materials [Hall and Hoff, 2009]. Electrical current follows the path of least resistance. When a rock matrix is considered non-conductive, the pore space is the only conductive element. Therefore, a well-connected pore space will result in a lower impedance compared to a less connected pore space [Schön, 2015]. The impedance is then also dependent on the content of the pore space, such as moisture saturation and ion content. Impedance will be decreased if a continuous path of moisture is present between the electrodes, as air is less conductive than water. The impedance will be further decreased if there are salt ions present within the solution [Hall and Hoff, 2009]. In Table 2.1 typical resistivity ranges for sandstone, fresh water and salt water are presented.

Table 2.1: *Typical resistivity range for selected materials from Palacky [1987]*

Material	Typical resistivity range [Ωm]
Sandstone	50-10,000
Fresh water	2-100
Salt water	0.2-1

From this table it is clear that electrical resistivity (and therefore impedance) can be used to distinguish between various solutions within a sandstone sample, as there is many orders of magnitude differences between the materials presented. The resistivity needs to be considered over the length between electrodes to become an absolute value. The range illustrates that there are several variables to consider, such as moisture content for the rock, salt content in the waters as well as temperatures and humidity [Lehmann, 2018].

Impedance can be measured using Electrochemical Impedance Spectroscopy (EIS). EIS is a non-destructive technique that applies an alternating current (AC) to a system and measure the response [Lasia, 1999]. This is preferred for measuring salt movement as applying a direct current would desalinate the object to be measured, affecting the measurements as they are taken.

EIS can be done at a range of frequencies or at a single frequency. If the interest is to make snapshots of a system over time (and the system is not connected continuously to the potentiostat), it can be more beneficial to use a single frequency measurement [gamry.com, a].

EIS is a very sensitive technique, which creates variations in measurements. These variations become larger when the resistivity increases [Lasia, 1999]. As such, consistency in data will increase as the impedance is lowered. This is further discussed in Section 3.4.3. Any variations in environment, type of stone, size and shape of object, salt type and concentration will affect the electrical properties of any object.

Impedance has successfully been used for moisture monitoring in Lehmann [2018], but has not previously been investigated for monitoring salt content or salt removal treatments.

3 Standard laboratory methods used in this study

3.1 Introduction to chapter

This chapter outlines the methods and analysis techniques that are used throughout this study. This includes preparation and characterisation of samples, application of ED and measuring impedance, together with the analysis process that samples undergo after treatment. The determination of what salt to use throughout this project is also discussed.

Electro-desalinisation (ED) should affect the following characteristics of the sample (see Section 2.2.1):

- The salt content of the pore water will change due to electromigration, and hence the electrical properties of the pore water
- The water content will decrease due to electro-osmosis and evaporation
- pH may change due to migration of H^+ and OH^- ions

Above effects may cause changes to the minerals within the sample. Therefore, to constrain any changes due to ED, the material to be treated needs to be properly characterised. The sample porosity, pH, conductivity as well as water and salt content of the samples needs to be measured before any form of ED treatment takes place.

There are two ways to analyse the effects of ED: non-destructive testing and destructive testing. Destructive testing involves destroying the sample to measure the effects of ED on the fragments.

Analysis of leachate from powdered samples enables accurate quantification of the salt content after treatment (conductivity, ion content), and indicates if there has been any chemical damage (pH, mineralogical change). In this study IC (Ion Chromatography) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) has been used for ion measurements. The mineralogical differences could be assessed using XRD, but due to Covid-related lab closures XRD was not used in this thesis.

Ideally each sample would be characterised using varying ED parameters (salinity, current etc.), however if destructive testing takes place the same sample cannot be used twice. This therefore requires multiple samples to be tested that are similar enough so that any differences can be ascribed to ED rather than the natural heterogeneity of the rock. For instance: variations in grain size distribution could affect flow properties; variations in mineralogy may affect impedance, flow properties and the way any damage is accrued in the rock (e.g. if different minerals are prone to damage in different ways).

Non-destructive testing would allow the same sample to be repeatedly tested, but this would only be valid if the residual effects on the sample of each test could be completely removed. As an example, if a first cycle of ED left a residue in the pores that could not be effectively removed, this would change starting porosity and resulting flow properties and may mean that results from a second cycle of ED were indicative more of the 'new' porosity than of any change in parameters such as initial ion content of the water. For this reason the majority of experiments here are destructive.

3.2 Characterisation and preparation of samples

In order to test a large number of samples, the samples should be relatively small so that treatment times are low, while still being large enough to handle easily for analysis. Previous studies showed successful desalination of samples with a thickness around 5cm. Herinckx et. al. [2011] were treating samples of 4cm thickness for 6 days with 2mA. Another study used samples that were 5cm thick and were treated with 2mA for 10 days [Matyščák, Ottosen and Rörig-Dalgaard, 2014]. A third had 6cm thick samples, treated with 3mA during 7 days of treatment [Feijoo, Ottosen and Pozo-Antonio, 2015]. The samples in this study were therefore chosen to be $5cm$ thick cylinders, with a diameter of 5cm.

The samples were made as cylinders using a 5cm core drill from slabs of rock. This provided a quick and effective way of making multiple samples with identical geometry, as the slabs were of a consistent 5cm thickness. Several slabs were used for the Clashach samples and one slab was used for the Stanton Moor samples.

The height and diameter of each individual sample was measured using a caliper placed at two different places for each measurement and averaged. Electrical current was applied to the entirety of the flat sides of the cylinders. Therefore the area used in calculations concerning the electrical flow is the cross sectional area of the cylinder, 1963mm^2 or 0.002m^2.

The porosity of the samples is a key characteristic of interest for this study. The samples were vacuum saturated with various solutions for individual experiments. Finally, the water content procedure is described.

3.2.1 Porosity

A material's capacity to transmit water is directly linked to its porosity. This can be non-destructively tested on each individual sample before treatment by the use of the Archimedes Mass method.

First, the sample is dried at 105°C until a constant weight is achieved. The sample's mass, m_{dry}, is recorded. The sample is then vacuum saturated with ultra pure de-ionised water, the procedure of which will be further described in the next section. Next, the saturated sample is weighed under water, $m_{underwater}$, as in Figure 3.1. The sample is then weighed out of the water water after any surface water has been gently removed, m_{wet}. To ensure no material was removed during the process, the sample is dried out again at 105°C to compare the dry weights before and after the process. The calculations for porosity, ϕ are as follows:

$$\phi = \frac{m_{wet} - m_{dry}}{m_{wet} - m_{underwater}} \tag{11}$$

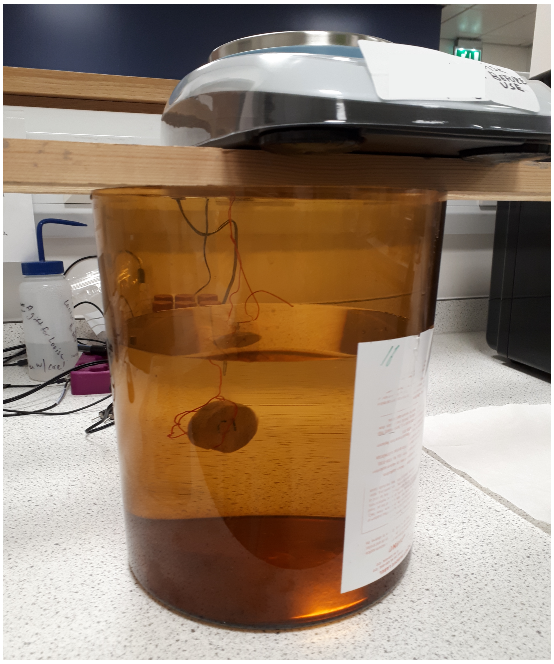


Figure 3.1: *Sample weighed under water*

3.2.2 Capillarity

Capillarity can also be investigated non-destructively and combined with the porosity data it can indicate the nature of the pore structure.

The sample is dried until constant mass. The geometry (height, diameter) of the sample is recorded. Metal rods are placed in a tray of de-ionised water, where the water reaches a few millimetres over the rods. The sample is placed on top of the metal rods, where a timer starts as soon as the sample touches the water. The sample is then weighed at a time interval of 1,2,4,8,16,32,60, and 120 minutes. The surface water of the sample is removed before the weight is noted, by gently dabbing it with a cloth. The data is then compiled into a graph, which slope indicates the pore size distribution of the samples.

3.2.3 Vacuum saturation

Throughout this study, stone samples have been tested at a range of different moisture saturations. Vacuum saturation is a quick and effective method to completely saturate samples with water or salt solution. This method is essential to ensure that all pores are saturated for investigating material properties such as porosity. Complete saturation through this method provides a uniform starting point for experiments.

The samples are first put in an oven at 105°C until they reach constant mass. The samples are then weighed (grams, to two decimal places) and placed in a glass desiccator. Glass is used in preference to metal to avoid issues of the salt rusting the material.

Once the samples are placed in the desiccator, the vacuum is connected, and is left on for three hours. After this, the valve to the desiccator is closed, keeping the vacuum within. The pipe connected to the valve is then filled with liquid to minimise the amount of air leaking into the vial once the valve is open. This results in the liquid being sucked into the desiccator and once the samples are covered with at least two centimetres of liquid, the valve is shut, maintaining the vacuum within the desiccator. After an hour the valve is opened and the samples are left at atmospheric pressure overnight. Figure 3.2 shows samples during the saturation process.

Figure 3.2: *Vacuum saturation in progress*

The samples are then placed in the same liquid in which they were saturated and kept in an airtight container preventing evaporation for later use. In this project, the vacuum saturation method was used with both ultra pure de-ionised water and different salt solutions.

3.2.4 Water content

Throughout this study, measuring the water content of samples was required for two purposes: to calculate the sample porosity and to calculate the saturation (or proportion of that porosity that contains water).

The water content test consists of weighing the sample, putting it in an oven at 105°C, and weighing the samples at intervals until the mass is constant. These measurements take between 15 and 30 minutes: the samples need to cool down so that they are safe to handle; the time needed varies dependent on the material and the size of samples. The final weight of the sample m_{dry} is subtracted from the weight recorded before the sample was put in the oven m_{wet}, resulting in the weight of the water that was present at the start, u.

$$u = \frac{m_{wet} - m_{dry}}{m_{wet}} \tag{12}$$

Sometimes, a water content test was not practical, for example during an experiment. In which case, the water content was estimated by calculating difference in weight at known time points.

3.3 Applying electro-desalination to stone

A step-by-step guide on how to administer ED in a lab has been developed in this study and can be found in Appendix 1.

3.3.1 Sample prep

The following list outlines the steps for preparing a sample for ED treatment which have been expanded in this study. This is further described in Section 5.1. Once these steps are completed, the electrodes are connected to a power supply, and electrical current applied. Once the wires are connected to the power supply, the system should not be touched. If anything needs to be adjusted, the power supply must be turned off off before touching to avoid electrical shocks to the user. These steps are also illustrated in Figure 3.3.

1. Make clay in accordance with recipe below
2. Prepare clay form to fit samples, insert one electrode
3. Wrap sample in cling film, leaving areas for electrodes exposed
4. Place silk paper on exposed areas of sample
5. Place clay forms and electrode on sample
6. Fill up clay forms with clay, specific to electrode
7. Place second electrode on top of clay
8. Wrap the clay and form in cling film
9. Repeat for second set of electrodes

In this study, the power supply used was a Cleaver Scientific Ltd., Power Pro 300. The maximum effect that it can provide are 300V, 700mA and 150W.

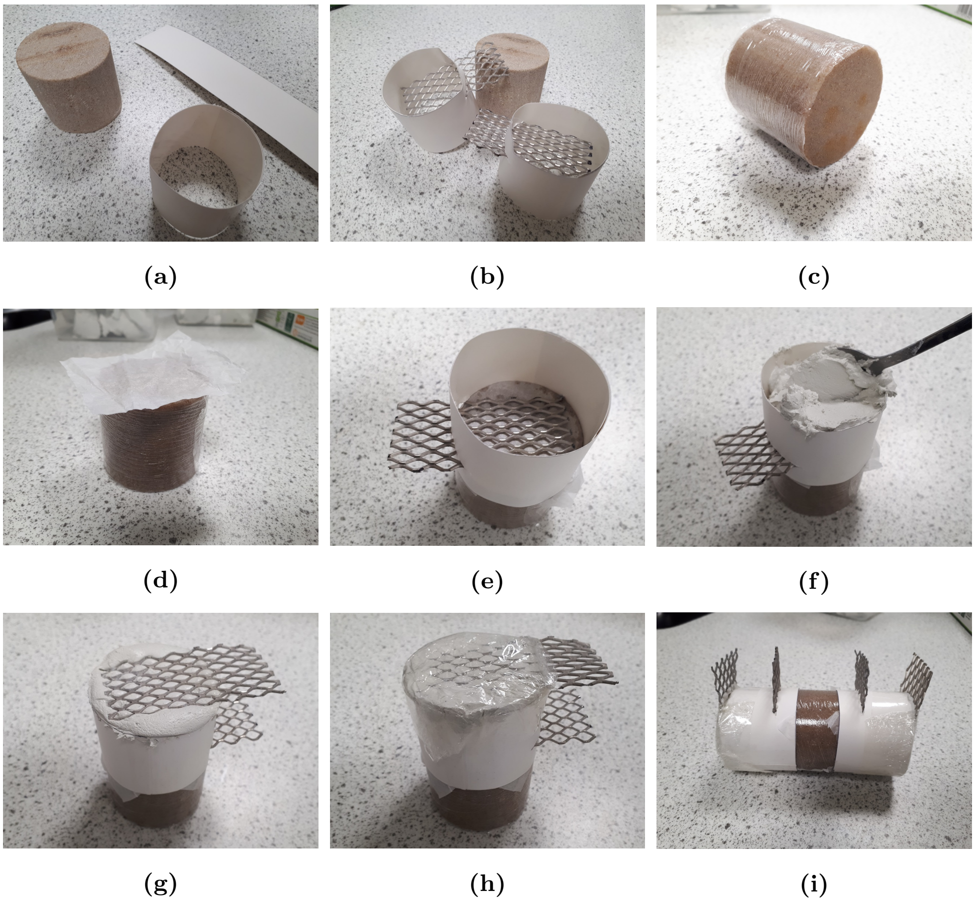


Figure 3.3: *Pictures of sample preparation for ED. a) Clay form making. b) Attaching inner electrodes to clay forms. c) Sample wrapped in cling film, sides exposed. d) Placement of silk paper. e) Placement of clay form. f) Filling up of clay. g) Placement of outer electrode. h) Wrapping electrode and clay in cling film. i) Repeated on other side, the finished system.*

3.3.2 The poultice clay

The purpose of the poultice clay is threefold; it provides a malleable interface between electrodes and stone, it absorbs the salt removed from the stone and it can be used to neutralise pH changes from the effects of the ED treatment (Section 2.2.3). Therefore, it is important to use a clay recipe which is both workable and absorbent. It is also desirable that is consists of standard ingredients in order to have a method that is easily accessible for application.

In their patent Rörig-Dalgaard and Ottosen [2009] suggest Kaolin clay because of it being pure, workable, does not shrink and is conductive when water is added. They also state a 40% water content for ideal consistency. They also present a variety of additives to prevent pH changes, including the recipe presented below that is used to prevent acidification at the anode. Rörig-Dalgaard [2013] has since investigated the efficiency of different poultices and showed that this is the most important poultice for a successful desalination. In order to keep the method application simple, this study will only use this recipe with added $CaCO_3$ for the anode. As there is no acid to neutralise at the cathode, the poultice used there is kaolin only.

Anode

- $200g$ Kaolin
- $400g$ $CaCO_3$
- $400g$ DI water

Cathode

- $600g$ Kaolin
- $400g$ DI water

The procedure of mixing the poultices was as follows: The dry components of the clay were put in a mixer bowl, and the water was added slowly while mixing to ensure optimal blending of the ingredients. Once the consistency was even the poultices were placed in air-tight boxes until they were to be used.

The plastic poultice forms were made to be the same diameter as the sample, and were 4cm long. When placed on the samples the total depth of the poultices was 3cm, as one cm was used to hold the form in place around the sample. There needs to be enough of depth to the poultice so that any acid created at the anode electrode is buffered before it migrates into the stone. 3cm has previously been efficient [Ottosen, Dias-Ferreira and Riberio, 2015], and the pH of the poultice clay was measured after each experiment to ensure that this was the case.

To avoid any variations in data based on the sample assembly, the clay must be packed thoroughly, as any air bubbles within could affect the impedance measurements.

3.4 Measuring impedance

3.4.1 The equipment

A potentiostat from Gamry instruments, the Interface 1000B, is capable of executing several electrochemical techniques. In this study, it is used for Single Frequency Impedance Spectroscopy that measures impedance at a specific frequency [gamry.com, a; gamry.com, b].

3.4.2 The approach

Single frequency data is used to investigate the change in impedance over time, and Lehmann and Krüger [2014] found 1kHz to be a useful frequency for both wet and dry samples. This frequency was therefore used throughout this study for impedance measurements.

The impedance of an electrical cell can be measured using two, three or four electrodes. When using two electrodes, the impedance of the entire cell is measured. When using three, half the cell is. Using four electrodes enables the possibility of measuring the impedance at two given points within the electrical system, independent of the position of the electrodes that applies the electrical current. The four electrode approach is illustrated in Figure 3.4 [gamry.com, c].

In this study, a method has been developed to measure impedance on samples undergoing ED

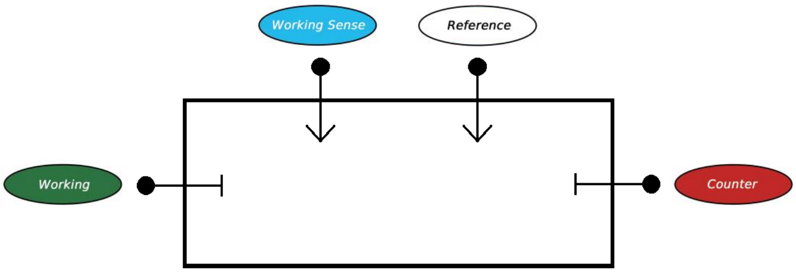


Figure 3.4: *4-electrode setup for measuring impedance on solid-state cells*

treatment in the lab using a 4 point setup. Figure 3.5 shows a sample set-up in the potentiostat with all the sensors attached to the appropriate electrode. The method is further explained in Section 5.1.

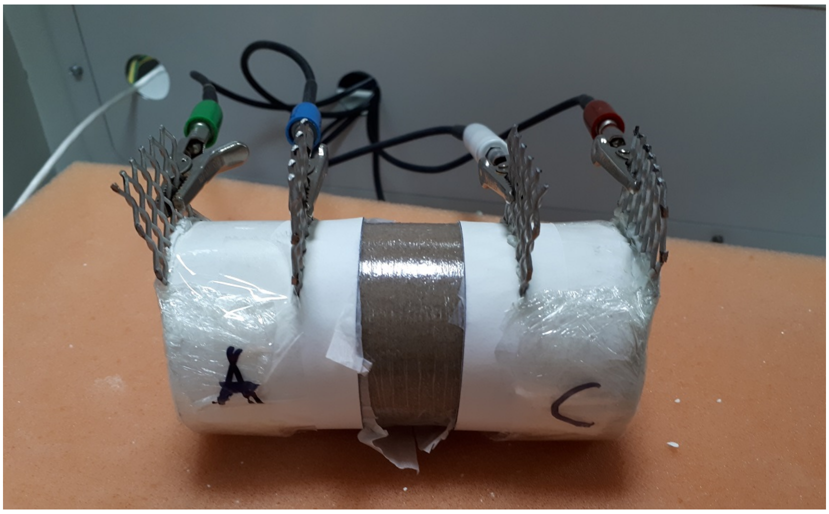


Figure 3.5: *A sample set-up in the potentiostat with all sensors attached to the electrodes embedded in the sample system*

The sample prepared as described in Section 3.3 was put in a Faraday cage, to prevent disturbance from surrounding electricity. A single frequency measurement at 1kHz was run and the sample was then disconnected from the potentiostat and removed from the Faraday cage.

3.4.3 Validity of measurements

In order to evaluate if the electrical impedance measurements are valid, Lasia outlines four criteria that need to be fulfilled; Linearity, Causality, Stability and Finiteness. This means that the data must follow a linear equation with only reasonable amounts of noise, that a stable system provides stable measurements that do not change over time unless the system does and finally that the measurements are constant real values, between zero and infinity. Should the measurements not reach these criteria they should be discarded [Lasia, 1999].

Lasia [1999] also states that impedance is a good precision measurement between 0.001 and 100 kΩ, but that distortions in the data occur at higher or lower impedance values.

Any variability in measurements is likely to be attributable to one or more of the following; inherent measurement error, assembly of the sample's treatment system or changes within the samples.

3.5 Analysis process

After ED treatment and impedance measurements, the samples undergo an analysis process which provides data concerning the sample's water and salt content. This process is described chronologically here.

3.5.1 Cutting

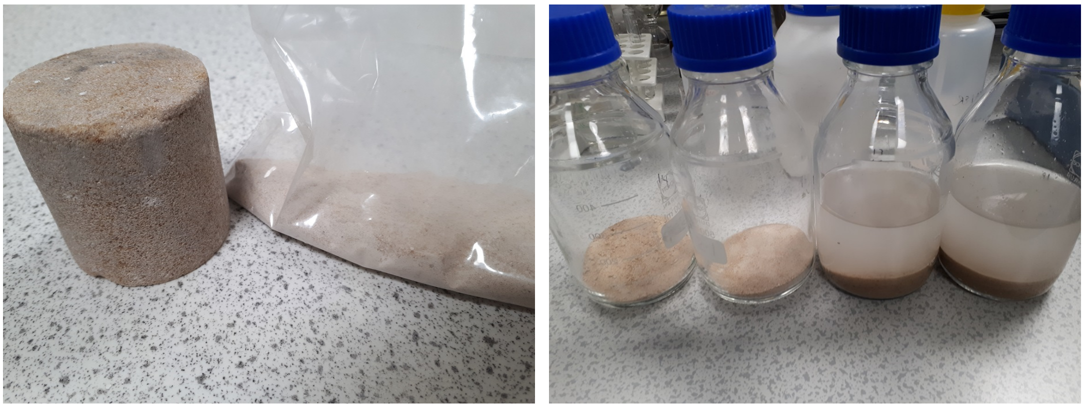
First, the sample was weighed. It was then cut into four 1.25cm slices by chisel. A saw would introduce either water or heat to the samples and possibly affect the measurements: salt could leach out with the added water; damage to the stone could come from the heat if water is not used. The slices were marked by a marker all the way around the cylinder. This marker was then followed by the chisel with tempered hits by the hammer until the entirety of the circumference had been hit. This was in order to create cracks within the sample that helped create even slices once it broke off. Once these cracks had been established, heavier hits was invoked until the sample separated. It was easier to first do the halves, then the quarters. The slices, or pieces thereof, were placed in petri dishes, weighed, and then placed in the oven for water content calculations (Section 3.2.4).

3.5.2 Leaching

The dried slices of samples were placed in a crushing device, operated by experienced lab technicians, and ground until 95% of the grains were less than 4mm [DTU, 2016], see Figure 3.6a. The crushed samples were marked individually and were then used in their entirety for leaching. This method provided the absolute value of salt within the sample.

Duran bottles of 100ml were first weighed and then a crushed sample slice was placed within. The bottle was then weighed again to provide the mass of the sample. Using the ratio of 10g of sample to 25ml of water, ultra-pure DI water was added to the bottle, see Figure 3.6b. The bottles were then placed on a shaker for 200rpm for 24h.

The next day, the bottles were removed from the shaker and left to settle. The leachate was decanted leaving residue in the bottle and the leachate was divided into three separate 50ml test tubes. One was for IC, one for ICP and one for pH and conductivity, see Figure 3.7a.



(a) (b)

Figure 3.6: *a) Leaching preparations with two samples, one intact and one crushed into sand. b) Samples in vials, without and with added de-ionised water.*

To facilitate the next steps of of the analysis process, the tubes aimed at IC/ICP analysis were put though a centrifuge (fx. 400rpm, 10min), forcing the bigger particles to settle in the bottom of the tube, see Figure 3.7b. The samples to the left are stone samples, before and after centrifuge and the samples to the right are clay samples before and after centrifuge. Notice the difference in residue build up after centrifuging.

(a) (b)

Figure 3.7: *a) Decanting the leachate solution into separate test tubes. b) Samples before and after centrifuging. The two tubes to the left are a stone samples; the two samples to the right are a clay sample.*

3.5.3 pH and conductivity

The leachate was measured for pH and conductivity. pH indicates chemical changes to the sample and conductivity was used as an indicator of salt content, which was needed for the subsequent IC/ICP analysis. In this study a Thermo Scientific Orion Star A215 was used, which can measure these properties simultaneously, reducing analysis time. Before starting measurements, it was important to calibrate the equipment. For both measurements, a probe was inserted into the leachate, avoiding contact with both the container and any built up residue in the bottom of the container. The container was swirled while measuring, and the probes were rinsed off with de-ionised water between each measurement. When the same sample was measured for both pH and conductivity, conductivity was measured first, as it is more sensitive to any contamination between samples.

3.5.4 Salt content measurement - IC/ICP

IC (Ion Chromatography) and ICP (Inductively Coupled Plasma) are two analytical methods that can be used to measure ions. In the Civil and Environmental Engineering lab at Strathclyde, the most common use is to measure negatively charged anions in the IC and positively charged cations in the ICP. The equipment used was a Metrohm 850 Professional IC system and a Thermo Scientific iCAP 6200 Duo View ICP Spectrometer, which is an OES (Optical Emission Spectrometry) type of ICP. For this project, the sample preparation was done by the author and the measurement of ions using the IC and ICP instruments was made by expert technicians.

The detection limit for IC is 1-5μg/L, with a relative standard deviation of 3% [Lemmon, 2001]. The ICP has a 1-100μg/L detection limit and 1-2% relative standard deviation [Thompson and Walsh, 2012]. For increased precision, IC and ICP sample aliquots should be made from the initial sample in duplicates, or even triplicates if enough material is available. The data presented in this study have been produced through duplicates.

The leachate to be used for IC/ICP analysis must be filtered through a 0.45μm filter before entering the instruments which are very sensitive to particles. Filtration can then be done either using a vacuum filtration system, or by hand syringe, as shown in Figure 3.8.

(a) **(b)**

Figure 3.8: *Filtering systems (a) by hand (b) using vacuum*

After filtration, samples were diluted. For the two instruments, vials, dilution liquids and standard ranges differ. For IC; specific tubes, ultra-pure DI water were used and the standard range is 0.1-10mg/L. For ICP; 15ml test tubes and 5% HNO_3 were used, with a standard range of 0.5-50mg/L for detection.

3.6 Determination and detection of salts

3.6.1 Rationale

As presented in Section 2, a variety of salts are of relevance to heritage stone. In order to minimise the variables during method development, this thesis focused on a single salt, $NaCl$. Sodium chloride is one of the most common salts known to damage building stones, and there already are several studies on sandstone and $NaCl$ that focuses on success of the treatment [e.g. Feijoo, Ottosen and Pozo-Antonio, 2015; Ottosen and Christensen, 2012; Rörig-Dalgaard, 2013].

3.6.2 Salt concentration

Most studies concerning ED have been using the Austrian Standard Önorm [1999] to evaluate success in treatments. This standard is considered to be on the safe side for evaluating masonry in general, and is presented in Table 3.1. For comparison, 1wt% is equal to 10mg of salt per g of stone.

Table 3.1: *Standard for salt levels influence on masonry from Önorm [1999]*

Önorm (1999)	Sulphate [wt%]	Chloride [wt%]	Nitrate [wt%]
No action needed	< 0.1	< 0.03	< 0.05
Individual assessment	< 0.25	< 0.10	< 0.15
Action needed	> 0.25	> 0.10	> 0.15

Another standard is suggested in Arent and Seele [2000], which corresponds to the levels presented in Önorm [1999], with the addition of two more levels, one lower and one higher. As extreme values in either direction have not been of interest for this work, the standard salt levels from Önorm [1999] have been used to evaluate treatments in this thesis.

The Önorm [1999] standard is used together with the average mass and accessible pore volume of 20 Clashach Sandstone samples to calculate what concentrations of Sodium Chloride to consider in this study. Concentration is here expressed as molality, denoted m, which is the moles of a solute per kilograms of solvent, or mol/kg.

In order to compare findings to the Önorm [1999] standard, four concentrations were examined, as shown in Table 3.2. One at the accepted level ($0.2m$), one in the contested range ($0.5m$), one unaccepted ($1.0m$), and one extreme ($1.5m$). The right column of weight percent can be directly compared to the middle column in Table 3.1.

Table 3.2: *Concentrations of Sodium Chloride used in this study*

Concentration	Molality (m) [mol/kg]	Weight percent [wt%]
Accepted	0.2	0.03
Contested	0.5	0.8
Unaccepted	1.0	0.16
Extreme	1.5	0.24

The salt content of a sample can either be measured using IC/ICP (Section 3.5.4) or be calculated when the sample is first saturated with a salt solution. The increase in mass for the sample before and after saturation is the mass of salt solution that is absorbed by the sample. The salt content of this solution is known. The percentage of salt compared to water can therefore be used to calculate the exact amount of salt that should be contained within the sample.

4 Material properties

4.1 Established properties of sandstones used

This study concerns the use of Clashach sandstone which has a pure mineralogy and a uniform pore size. These attributes minimises variables during experiments. It is also a common building stone used in new build and conservation projects throughout Scotland. A comparison is also made with Stanton Moor sandstone, which has a higher clay content and higher porosity than Clashach. It is throughout Scotland for new build construction projects. The two stones' mineralogy, porosity and pore size distribution is shown in Table 4.1, Table 4.2 and Figure 4.1, data taken with permission from Graham [2016].

Table 4.1: *Mineralogy and average porosity of materials*

Stone type	Quartz [%]	K-Feldspar + mica [%]	Fe-oxide + other [%]	Clay/cement [%]
Clashach	83.9	1.2	1.6	3.3
Stanton Moor	73.5	3.5	2.0	7.0

Graham used mercury porosimetry, helium porosity, water buoyancy and SEM to characterise the pore structure of each sandstone. Presented in Table 4.2 is the average for the relevant sandstones, together with the standard deviation and variation.

Table 4.2: *Average porosity data using several methods and calculated effective open porosity from Graham [2016].*

	Porosity [%]	Effective Open Porosity [%]	SD	Var
Clashach	10	6	0.8	8.2
Stanton Moor	14	12	1.5	11.1

Clashach sandstone has a lower porosity then Stanton Moor sandstone, and has a lower variation between samples. Graham also measured the sandstone's pore size distribution, using mercury intrusion porosimetry (MIP). The mean of three samples is presented in Figure 4.1.

The pore size distribution for Clashach sandstone is quite uniform, with 73% of pores being between 10-50μm, whereas Stanton Moor sandstone is more evenly divided between 0.1 and 10μm.

To summarise, Graham [2016] has measured many properties of the sandstones used in this study. Clashach contains more quartz and less clay than Stanton Moor, is less porous and has a more uniform and smaller pore size distribution, with greater proportion of large pores.

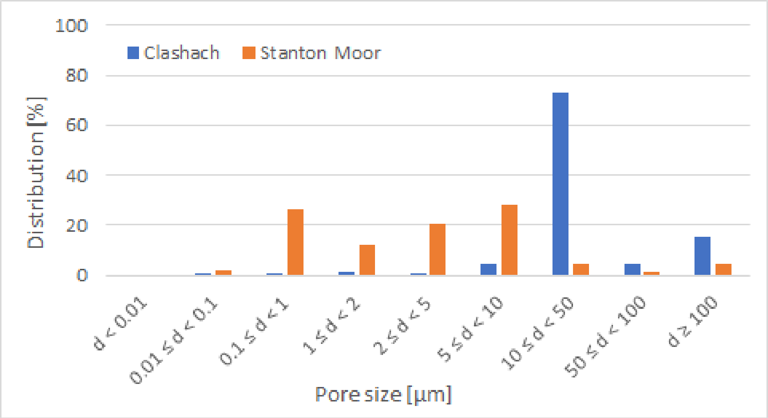
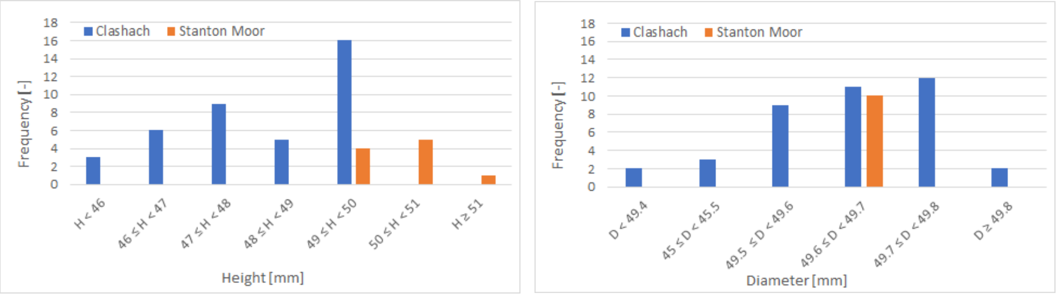


Figure 4.1: *Pore size distribution [d] of Clashach sandstone (blue) and Stanton Moor sandstone (orange) from Graham [2016].*

4.2 Height and diameter of samples

The height of the samples determines the minimum length of the electrical current's path between electrodes. The sample height should be relatively uniform as the samples have been cored from slabs of stone. The diameter of the samples determines how much electrical current to apply, as the current density is defined as the amount of current applied over the cross sectional area (A/m^2). A larger diameter will require more electrical current to ensure the same effects. As the samples are all cored with the same 5cm drill, the diameter is also expected to be relatively uniform.

Both the height and diameter have been determined using calipers, and each measurement taken twice (Section 3.2). The results of these measurements are presented in Figure 4.2.



(a) **(b)**

Figure 4.2: *Measured height [H] in Figure a and diameter [D] in Figure b for 39 Clashach Sandstone samples (C1-C39) and 10 Stanton Moor Sandstone samples (s1-S10) used in this study. The variations in the measurements can be attributed to their preparation, further addressed in Section 4.4.*

The height of the samples are more varied than the diameter, which can be explained by the use of the same core drill, while slabs of stone might vary in thickness. The larger spread in Clashach is because they were cut from several slabs. The Stanton Moor samples were cut from one, slightly thicker slab than the Clashach samples which helped to maintain consistency in their height.

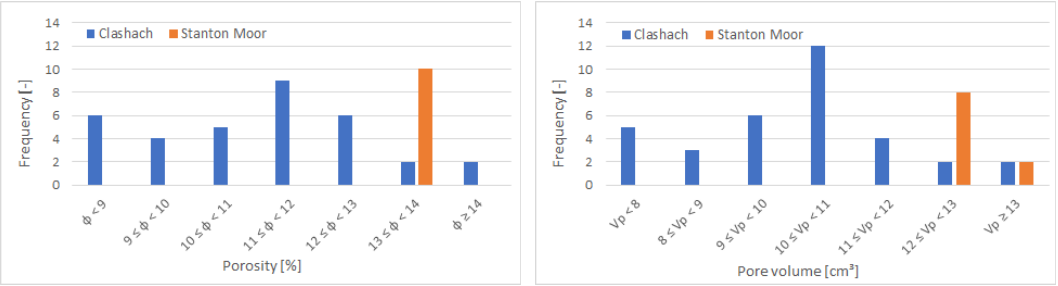
The average height and diameter for the two sandstones are presented in Table 4.3 together with standard deviations.

Table 4.3: *Median and standard deviation for the samples used in this study. n.b. the data for the Clashach sandstone is quite skewed so the mean is not the best average to take*

Rock type	Height [mm]	Diameter [mm]
Clashach	48.09 ± 1.34	49.64 ± 0.12
Stanton Moor	50.13 ± 0.42	49.66 ± 0.01

4.3 Porosity and pore volume of samples

Using the Archimedes principle, described in Section 3.2.1, the porosity and the pore volume of the samples can be calculated, and is presented for all samples used in this study in Figure 4.3.



(a)

(b)

Figure 4.3: *The porosity [ϕ] in Figure a and pore volume [Vp] in Figure b of all Clashach and Stanton Moor samples used in this study.*

The Clashach samples have a lower porosity and a larger range for porosity values than the Stanton Moor samples; this variability between the sample populations is further discussed in Section 4.4. The same variability is also seen in the pore volume, as is expected. As the pore volume is also lower for Clashach than for Stanton Moor, Stanton Moor can absorb more water, which needs to be considered when comparing saturation of the two stone types.

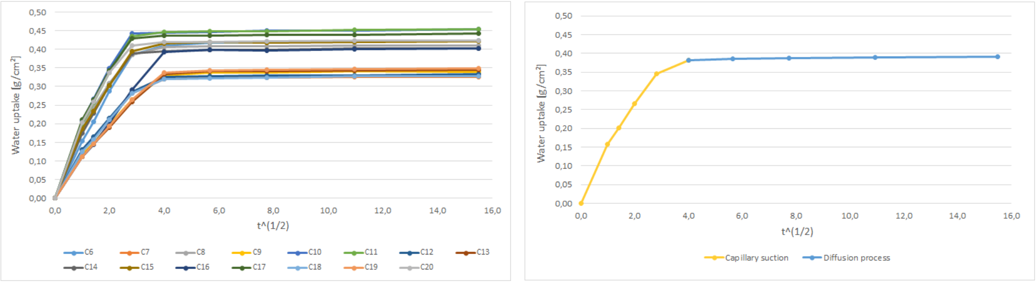
In this study, the porosity measurements are used as a basic property to be used for comparison between samples and types of stone. The pore space is used for saturation calculations in later experiments and dry weight is used as a reference point throughout the study. The median and standard deviation of these properties are presented in Table 4.4.

Table 4.4: *Porosity, dry weight and pore volume for Clashach and Stanton Moor samples*

Rock type	Porosity [%]	Dry weight [g]	Pore volume [cm^3]
Clashach	11.62 ± 1.73	207.50 ± 4.14	10.15 ± 1.61
Stanton Moor	13.24 ± 0.05	220.44 ± 2.43	12.78 ± 0.13

The porosity data gathered here can be compared with the data in Graham [2016]: Clashach 10% porosity, 0.8% standard deviation; Stanton Moor 14% porosity, 1.5 standard deviation. In both studies, Clashach is the less porous stone, but mean and standard deviations values do not match perfectly. This can be explained through the heterogeneity of stone, further discussed in Section 4.4. The variations within each stone type are greater for Stanton Moor in Graham's study, whereas it is the opposite here. This can be explained by this study using more Clashach samples than Stanton Moor samples, and that these Clashach samples were taken from several slabs of rock whereas the Stanton Moor samples were taken from only one.

Apart from porosity and pore volume, the capillarity of 15 Clashach sandstone samples (C6-C20) was investigated. This is done in accordance with the description in Section 3.2.2. The water uptake of all samples is shown in Figure 4.4a, where a difference can be seen for samples based on their porosity. The mean of all samples at each time point is presented in Figure 4.4b.



(a) **(b)**

Figure 4.4: *The water uptake for all samples 15 Clashach samples (a) and the mean of these samples with the two phases of capillary suction (yellow) and the diffusion process (blue) of water absorption marked on the curve.*

The change in absorption process from capillary suction to diffusion can either be very quick if the material's pores are mostly large and therefore uniformly filled at the same time, or slower if there is a bigger variety of pore sizes [DTU, 2016]. As is seen in the graph above, the change in process is very quick, indicating a uniform large pore size distribution. This is confirmed by the data gathered by Graham, presented in Figure 4.1.

4.4 Representativeness of samples

The samples were gathered using a core drill on 5cm slabs of sandstone (Section 3.2). The Clashach samples were cut from several different blocks at different times while the Stanton Moor samples were cut from a single block. It is likely that this will produce more consistent data in the Stanton Moor samples than the Clashach samples, as different blocks can come from varied parts of the quarry and therefore be quite different in properties.

4.5 Conductivity and pH for Clashach samples and clay poultices

Conductivity is used as an indication of salt content for IC/ICP measurements (Section 3.5.4) and pH is measured in order to rule out damage from pH changes (Section 2.2.3).

Two Clashach samples, one untreated and one saturated with 1m NaCl, together with an unused cathode and anode clay have undergone the analysis process described in Section 3.5, being leached in DI water and then have had measurements taken on this leachate. Each sample was divided into two before leaching, in order to undertake duplicate measurements. The results are presented in Table 4.5. Stanton Moor was not analysed for conductivity or pH during this study.

Table 4.5: *Conductivity and pH for Clashach and poultices*

Type	Conductivity [$\mu S/cm$]	pH [-]
1m NaCl sat. Clashach	2581.00	8.17
Untreated Clashach	55.78	7.51
Unused cathode clay	238.15	5.73
Unused anode clay	286.55	9.13

As expected, the NaCl saturated Clashach has conductivity two orders of magnitude higher than untreated Clashach. Untreated Clashach has a neutral pH, while NaCl infused Clashach has a pH under half a pH unit higher. The conductivity of the poultice clays is very similar, but they have a very different pH, with the cathode poultice being acidic and the anode poultice being alkaline. This is deliberate, as they are put in place to neutralise the effects of the electrolysis, where pH will increase at the cathode and decrease at the anode.

4.6 Salt analysis of control samples and clay poultices

Because they are naturally occurring compounds, various salts might be present within the stone samples or the clay used for ED treatments. The salt present in unused clay and Clashach samples has therefore been analysed using IC/ICP (Section 3.5.4), and is presented in Figure 4.5, as mg of ion per g of stone (1mg/g = 0.01%). For comparison, the salt solution that will be introduced to the samples, 1m NaCl, will result in a salt content of ca. 67mg/g (6.7%) of salt compared to the sample's dry mass.

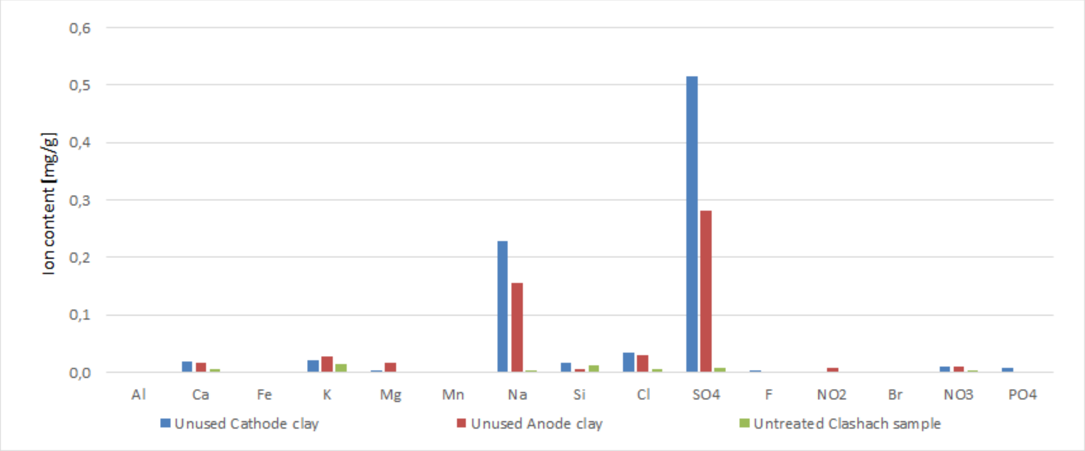


Figure 4.5: *Ion content for control samples of Clashach sandstone and unused anode and cathode clay.*

IC/ICP analysis is a lengthy and expensive method and it is desirable to minimise any unnecessary salt ion analysis. The ions $Al, Fe, K, Mg, Mn, Si, F, NO_2, Br, NO_3, PO_4$ all showed significantly less than 0.1mg/g, or less than 0.001% presence in the samples. Compared to the 6.7% of NaCl that will be introduced to the samples, these measured ions are therefore considered insignificant to affect any analysis made during the experiments and will therefore be disregarded in further analysis.

The two ions that were detected as more than 0.001% prevalent were Sodium (Na^+) and Sulphate (SO_4^{2-}), both present in the poultices. Sodium will be analysed regardless, as will Chloride (Cl^-). Sulphate is another potentially harmful ion [Ottosen and Hansen, 2016], although at a very low concentration here. In order to control that Sulphate is not amassing during the treatment, it will be included in the IC/ICP analysis throughout this study. The final ion to be considered for IC/ICP analysis will be Calcium (Ca^{2+}), as it is expected to be released as a result of acid buffering during treatment (Section 2.2.3).

5 Method development

This chapter presents method development on a new electrode set-up for ED treatment, including investigation into suitable strengths of electrical current. ED treatments during the early stages of this project provided information on the efficacy of poultices on the treatment and the effects of treatment on poultices during ED treatment and treating several samples simultaneously with the same power supply.

5.1 Electrode setup for impedance measurements

5.1.1 Initial setup

An experimental set-up was developed to be consistent with the simple and effective set-up developed by Rörig-Dalgaard and Ottosen (2009) at the Technical University of Denmark. In this set-up, the sample is placed in between two poultices each of which has a specific chemistry according to the electrode that is to be placed onto the poultice. The electrodes are placed on the outside of the poultices and the entire set-up is wrapped in cling film to prevent evaporation. This set-up is illustrated in 5.1.

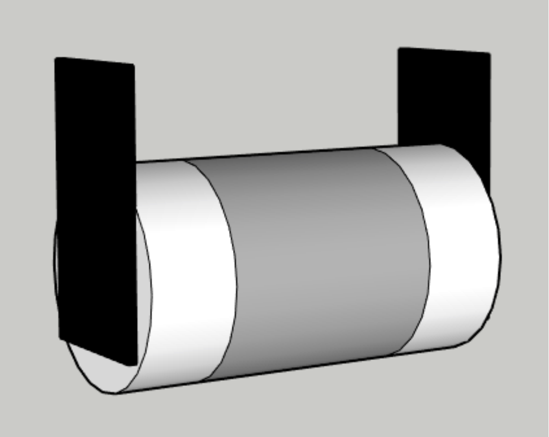


Figure 5.1: *Original electrode set-up. The sample in the middle (grey) is wrapped in cling film, excluding the flat surfaces at the ends. Silk paper is placed on the flat surface to prevent staining from the poultices as explained in Section 2.2.3. A plastic form is placed round the edge of the sample on each side, taped tightly to stay in place. The form is filled with poultice (white) and the Electrodes are placed on the outside of the poultice.*

A disadvantage of this setup is that it is not possible to detect what is happening within the different phases of the poultice-sample-poultice system during the treatment. For instance, the sample and poultices could have very different resistance, but this can not be measured in this set-up. If it was possible to measure the resistance across the sample alone, this measurement could be used to indicate the removal of salt from the stone into the poultice.

5.1.2 Developed technique

A new set-up has been developed that uses four electrodes instead of two, with a second set placed between the sample and poultices, shown in Figure 5.2. The outer set of electrodes is used to apply the electricity and the two inner ones are used for measuring across the sample using an external voltage meter, or potentiostat. This provides a way to monitor the change in resistance across the stone sample alone, rather than across the stone and both poultices together.

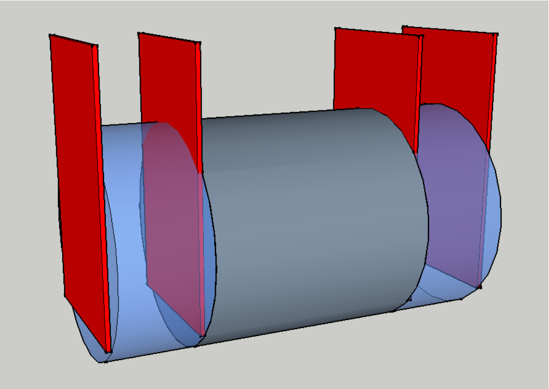


Figure 5.2: *Developed electrode set-up. As previously, but an extra set of electrodes are inserted between the sample and the poultices.*

The potentiostat is used to measure impedance, which in turn can be used to estimate the resistance of the sample (Section 2.3.3). This estimation can then be used to calculate the resistance from the poultices based on the potential difference across the entire system during treatment, as the system is connected in series, $Z_1 + Z_2 = Z_{tot}$. This would be a useful monitoring system of the desalination treatment, where the increasing resistance of the desalination system is either based on the sample becoming desalinated or the entire system drying out (or connections becoming poorer).

5.2 Strength of electrical field

In order to control the rate of ion transport throughout the treatment, an electrical current will be applied during ED in this study. Although several studies have been published on Electro-Desalination, the specific characteristics (electrical current and voltage) of a usable electric field have not been investigated in depth (Section 2.2.2). In order to present the ED method as a complete solution for desalination the limiting factor (maximum current) for safe application is investigated. The results are presented in this section, and a limit to the applied DC is established.

5.2.1 Calculations

In order to design the experiments for investigating the limits of applied DC, calculations of expected current densities for the geometry of the samples in this study in Table 5.1. The samples have a diameter of 5cm which results in a contact area with the electrodes of 19.6cm^2.

Table 5.1: *The equivalent current density for specified currents, for 5cm diameter contact area*

Applied current [mA]	1	5	10	20	30	40
Current density [A/m^2]	0.51	2.55	5.09	10.19	15.28	20.37

Liu and Shi [2012] suggested a maximum current density of 5A/m^2, but did not presented results that justified the rationale for this statement. For the samples in this study, that would be equivalent to applying 10mA across the sample.

The variable power supply used in this study can only supply power between 1V and 300V. The measurement of power is less accurate towards the lower potentials. The power supply's restrictions are 300V, 700mA, 150W.

5.2.2 Trials from this study

Finding an effective DC for successful ED treatment Sample C1 was saturated with 1m $NaCl$ and treated with 5mA, an arbitrary chosen electrical current. The ED treatment of C1 lasted for 6 days based on the previous monitoring method of noting potential difference (Section 2.3.1). A control sample (C2) was saturated with the same salt solution and directly processed for IC/ICP. These samples were processed according to the method used in Ottosen's lab, which provides an estimation of the salt content of the samples rather than an absolute value (Section 3.5.2). The reduction in salt concentrations is presented in Table 5.2.

Table 5.2: *Estimated salt content of an ED treated sample (C1) and a control sample (C2), based on IC/ICP measurements. From the entire sample (ca. 210g, only 40g has been analysed, the data of which is extrapolated to give the estimations presented here.*

Sample	C1 ED treated [mg]	C2 Control [mg]	Removal [%]
Cl	13	516	97
Na	3	297	99

From this data it is clear that 5mA is a high enough current density to remove the salt. The absolute amount of salt can not be calculated using the analysis process of Ottosen's lab and the data for these sample will not be investigated further. A different method for salt analysis has been used throughout this study, from sample C7 and onward, further discussed in Section 3.5.2.

Sample C6 was saturated with the same salt solution as C1 and C2, and treated with 5mA for 6 days. It was also set-up with the new electrode system described in Section 5.1. The impedance of the sample was measured before and after the ED treatment. The calculated initial and estimated final salt content is presented together with the impedance measurements in Table 5.3.

Table 5.3: *Salt content before (calculated) and after (estimated) and impedance measurements before and after ED treatment for sample C6.*

	Salt content before [mg]	Salt content after [mg]	Imp before [$k\Omega$]	Imp after [$k\Omega$]
C6	860	115	0.2	34.3

The salt content before treatment is calculated based on the mass of the salt solution that the sample was saturated with, and the final salt content was estimated using the same procedure as samples C1 and C2: by taking ten grams of the sample for IC/ICP analysis. For all experiments after C6, the entire sample was used for salt analysis by IC/ICP.

The reduction of salt content is 87%, corresponding to a factor of 180 increase in impedance. These results for C6 are used as an indication for impedance values that are representative for salt saturated samples (0.2kΩ) and desalinated samples (35kΩ).

Investigation of effects from high DC

Sample C7 was saturated with the same $1m$ $NaCl$ solution as the previous samples. It was also set-up using the new electrode system to enable impedance measurements. The readings of the potential difference for the three different ED treatments that the sample went through is presented in Figure 5.3.

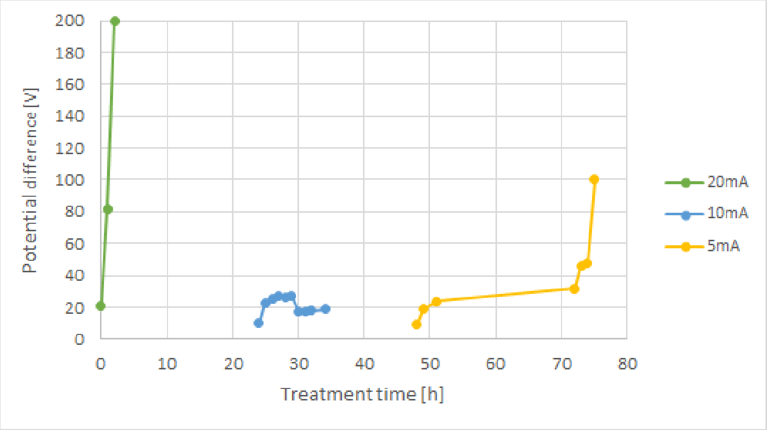


Figure 5.3: *Measured potential difference [V] of the system during ED treatments of sample C7. Treatment 1 (green): 20mA - 10A/m^2, treatment 2 (blue): 10mA - 5A/m^2, treatment 3 (yellow): 5mA - 2.5A/m^2*

Initially, 20mA was applied to the sample, four times higher than the previous sample (C6) had been treated with. A limit was put on the power supply to not exceed 200V, in order to keep a safe work environment. This treatment resulted in 200V being reached after only 2h, a very short treatment time. The increase in potential difference is the usual measure of completed desalination (Section 2.3.1). However, most desalinisation takes a week or weeks [e.g. Ottosen and Rörig-Dalgaard, 2009; Ottosen, Dias-Ferreira and Riberio, 2015], so it is unlikely that desalinisation has been achieved in such a short amount of time. The impedance of the sample only increased from 0.1kΩ to 0.2kΩ from start to finish. By comparing this to the impedance found for sample C6 in Table 5.3, it was assumed that the salt within sample C7 had not been removed.

Apart from impedance remaining low, the stone was warm to the touch (warmer than 37°C). This could affect both the impedance measurements and the resistance calculations. What may have been happening was that water movement due to electroosmosis (Section 2.2.1) was separating the water films within the pores, making it increasingly difficult for the electrical current to pass through the pore system. Disconnecting the water films within the pores would also retard salt ions from being removed. From this it could be concluded that a current density of 10A/m^2 or 20mA, is too high for ED treatment. Though this conclusion requires further studies to be verified.

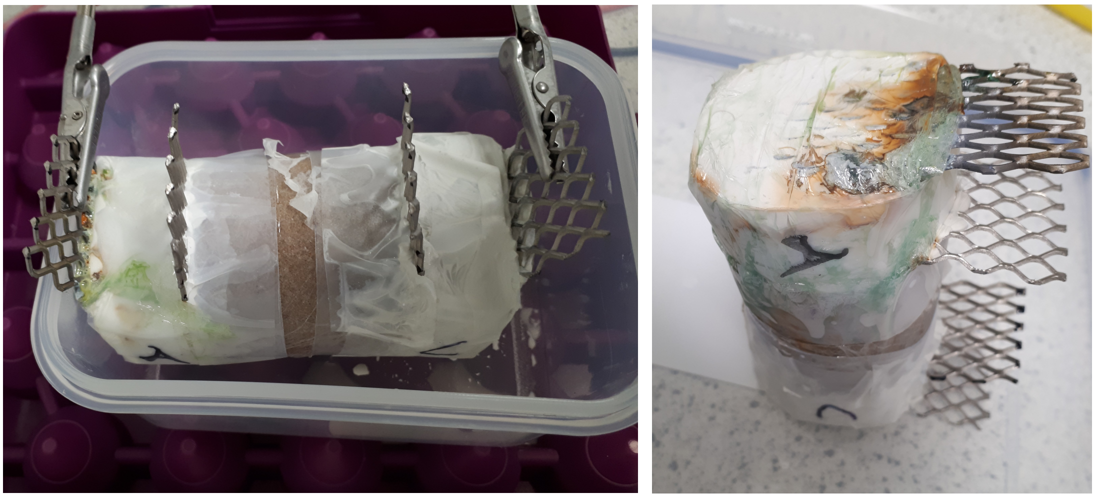
As desalination was not expected to have taken place for sample C7, it was set-up for a second ED treatment. The sample system was placed in a airtight box with the poultices detached from the sample over night to let any water separation even out within the sample. The day after, the second treatment started, using a reduced current of 10mA. This is still twice the current used for the previous samples.

Based on Figure 5.3, it seems like the ED treatment was progressing using 10mA. However, after 5h of 10mA treatment, something green started oozing out of the anode and a heavy stink of chloride was developing (Figure 5.4a). After a total of 9h treatment there was also severe corrosion at the anode electrode (Figure 5.4b) and the generation of chloride gas was continuing.

The treatment was carried out in a sealed box, as chloride gas is toxic. In a real world application, it would be unwise to apply a treatment that creates toxins at a high rate as well as destroying the electrodes. In order to prevent exposure to toxins, as well as electrode damage which would introduce new variables in the system, it was decided to stop the high current treatment.

The potentiostat was at this point not available for use, or an impedance measurement might have been able to be used for evaluating if salt was being removed from the sample. As there seemed to be a stable electrical connection throughout the treatment, it is assumed that the treatment was working. From this it can be concluded that while it is possible to use 5A/m^2 (10mA) for ED treatments, this risks endangering the user as well as damaging equipment.

Using new poultices and new electrodes, sample C7 was set-up for a third ED treatment using



(a) (b)

Figure 5.4: *Pictures of unwanted effects on the system of sample C7 from ED treatment using 10mA, an equivalent of 5A/m*^{2}*. a) Green ooze developing at the anode side of the sample during treatment. b) Corrosion at the anode electrode during treatment.*

5mA (2.5A/m^2), the same as previous samples in this study.

The development of potential difference in this instance (Figure 5.3) followed a similar progression to previous studies [e.g. Norsk and Andersson, 2016; Ottosen and Rörig-Dalgaard, 2009]. The impedance was at the end of the 5mA treatment 7kΩ, so complete desalination was not expected to have taken place. There was however a heavy chloride smell from the sample and there were signs of corrosion at the anode, so it was decided to stop the treatment of this particular sample.

Based on this trial it was decided that due to the potential risks and introduction of further variables, strength of the electricity field will not be further investigated in this study. All further experiments are treated with 5mA equivalent to a current density of 2.5A/m^2. To prevent potential harm to the user and other lab users, a limit to the applied voltage is set at 100V for future experiments.

5.3 The effects of ED on poultices and the influence of poultice exchanges

When applying ED, the poultices used are required for a) keeping a stable connection between electrode and stone; b) providing a reservoir for gathering the salts removed from the stone; and most importantly, c) acting as a pH buffer to prevent acidification (Section 2.2.3). Using the new monitoring system (Section 5.1) and the appropriate electrical current (5mA, Section 5.2), two experiments were run in order to investigate how electro-osmosis would impact the treatment (Section 2.2.1) and if it would be advantageous to exchange poultices during treatment.

5.3.1 Experimental design

Both experiments used the poultice recipes from Section 3.3.2: one with pure kaolin and water (cathode poultice), and one also containing $CaCO_3$ (anode poultice) to provide a buffer to prevent acidification (Section 2.2.3). An electrical current was applied and the voltage was noted hourly during work hours (8am-4pm) in accordance with the established method for monitoring the development of the treatment [Rörig-Dalgaard, 2013]. Once the potential difference increased to 100V the treatment was halted. During the treatment the sample systems were disconnected from the ED treatment in order to be weighed and measured for impedance, also hourly, before being re-attached to the ED treatment. The samples and the poultices were then processed in accordance with Section 3.5 and conductivity, pH and salt content were measured.

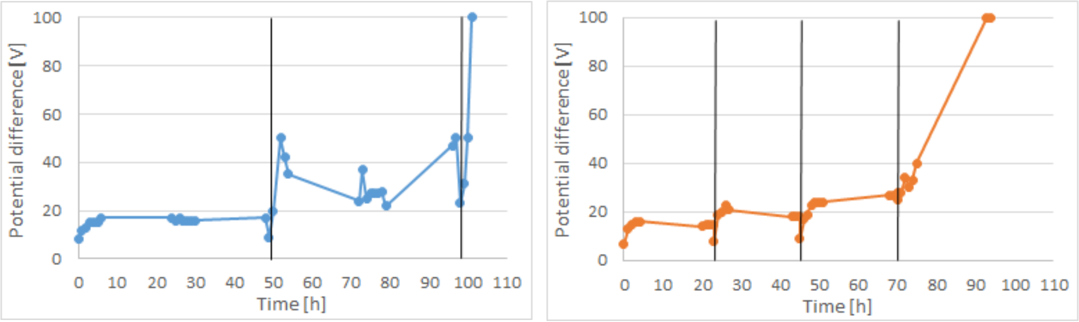
For this experiment, deviating from the method description in Section 3.3, the poultices at both anode and cathode were removed and replaced with new poultice clay; 3 pairs of poultices were used for C8 and 4 pairs for C9. The timing of these poultice exchanges is marked by vertical lines in Figure 5.5.

5.3.2 Results

The data gathered during these experiments are presented here. First the development of potential difference and moisture content for the experimental setup is presented, followed by the sample's impedance during treatment and their final values of water content, salt, pH and conductivity, and finally the data collected for the poultices.

Potential difference

The voltage development during the duration of the treatment is presented in Figure 5.5.



(a) *C8*

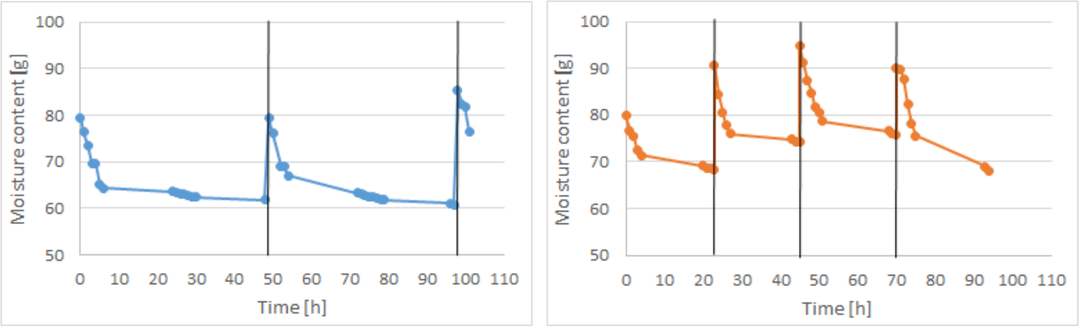
(b) *C9*

Figure 5.5: *Potential difference development during ED treatment of C8 (a) and C9 (b), both treated with 5mA. Poultice changes are indicated by vertical lines on the graph.*

For sample C8 (blue), the voltage assumes a stable level just under 20V during the first two days of treatment. After the first clay change the voltage becomes erratic, which could be for a number of reasons, which will be discussed further in Section 5.3.3. The final potential difference (100V) that has been accepted as indicating complete treatment is not reached until hour 101, after the second clay change. Sample C9 (orange) follows a smoother curve, slowly increasing over time until maximum voltage was observed at 93h. What is clear from both of these curves is that the voltage, and therefore the system's resistance is lowered directly after the poultices are exchanged.

Moisture content of systems

The moisture content of the system before treatment can be calculated using the water content in the poultices and the salt solution that was absorbed by each sample. As the only thing that can affect weight during treatment is the removal of water, thus the water loss can be calculated from the weight difference of the systems. The water content of the poultices is measured using the method presented in Section 3.2.4 once they are removed, and the residual water content of the sample can be estimated based on this. The estimation of water content for both sample systems during treatment are illustrated in Figure 5.6. The moisture content of the poultices are presented later in this chapter.



(a) *C8* **(b)** *C9*

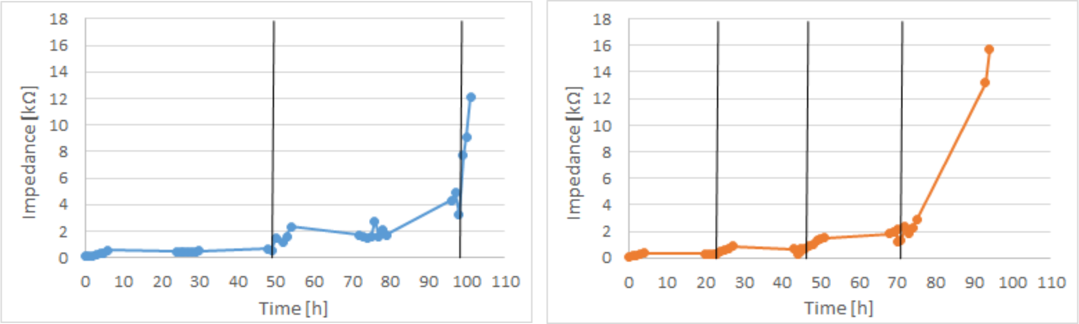
Figure 5.6: *Moisture content development of the experimental systems of C8 (a) and C9 (b) during ED treatment based on measured water content at clay changes and calculated using the total weight of the systems. Poultice changes are indicated by vertical lines on the graph.*

These is a clear pattern that emerges from these curves. The first hours after a new pair of poultices was attached to the sample resulted in rapid reduction of the weight (water) in the system. This can largely be attributed to water pouring out of the cathode clay compartments during the first hours of ED treatment. This is attributed to the water movement resulting from an applied electric field to a porous material, also called electro-osmosis (Section 2.2.1. When the clay was allowed to remain on the sample for longer (as for sample C8), a stabilisation of the water content reduction is seen. The difference in reduction rates between a slightly quicker decrease in moisture during day time compared to night time is likely due to the sample not being handled as much at night.

Impedance of samples

The impedance of the samples was measured during the ED treatment as an initial trial of the developed electrode set-up. The results are presented in Figure 5.7

In both cases, the impedance increases slowly over time, following a power law function. Based



(a) *C8* **(b)** *C9*

Figure 5.7: *Impedance measured for samples C8 (a) and C9 (b) during ED treatment. Clay changes are indicated by vertical lines on the graph.*

on the theory presented in Section 2.3.3, this is likely to indicate salt removal. Experiments that investigate the relationship with impedance and salt removal further are presented in Chapter 7.

Post-treatment analyses

One the treatment was concluded, the samples were processed and their final pH, conductivity, moisture content and salt content was measured. This data is presented in Table 5.4.

Table 5.4: *Values for samples after treatment; average pH, average conductivity, moisture and final salt content in relation to the samples dry weight*

Sample	pH [-]	Conductivity [mS/cm]	Moisture content [%]	Salt content [mg/g]
C8	8.56	0.20	4.53	0.03
C9	9.81	0.13	1.64	0.01

During ED treatment using a pH buffer to prevent acidification, an increase in pH is expected to take place (Section 2.2). This happens more for sample C9 than C8, this is likely due to the formation of more OH^- ions as a result of the more frequent clay change. As hydrogen ions are the result of water splitting at the anode due to electrolysis, adding fresh clay with more water will result in an increase in pH.

The moisture content of C8 is at 4.5% after treatment, which should not affect the ED treatment (Section 2.2.4). C9 has a moisture content of 1.6%, a third of that of C8. This is likely due to the application of new poultices, which induces an electro-osmotic effect (Section 2.2). Although no hampering of the ED treatment is expected to this moisture content, it would be more desirable to avoid water transport out of the system.

Both samples achieve desalination to below the accepted limit of 0.3mg/g of Cl^- ions (Section 3.6.2) [Önorm, 1999]. The salt content of the samples before and after the treatment is presented in Table 5.5, as is the reduction of salt as a percentage. With over 99 percent salt removed from both samples, the treatment is considered complete.

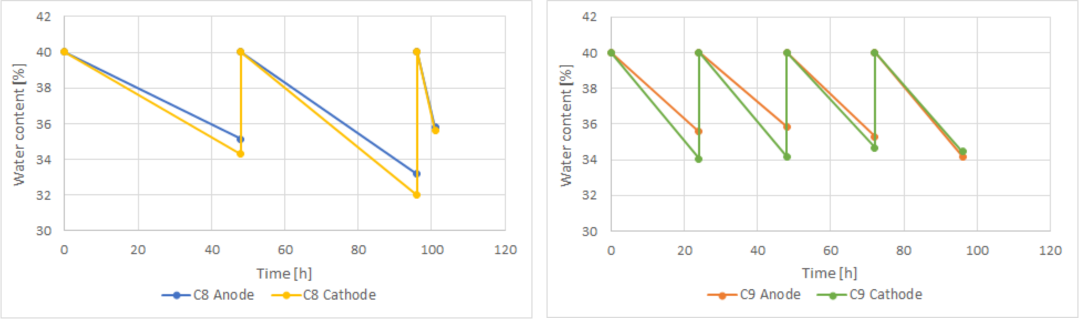
Table 5.5: *Salt content of samples before and after treatment together with the percentage of salt removal.*

Sample	Salt content before [mg]	Salt content after [mg]	Salt removal [%]
C8	774	6	99.2
C9	738	2	99.7

Clay data

During the treatment the poultice clay has been changed at different intervals. The measured water content (Section 3.2.4), pH (Section 3.5.3) and salt content (Section 3.5.4) of the clay poultices are presented here.

The percentage moisture content of the clay poultices after treatment is presented in Figure 5.8. The initial moisture content of all poultices is 40%. The water content is consistently lower after treatment, and the cathode clay contains less water than the anode clay for both samples. For the final data point, both clay compartments are very close to each other in water content. At no point does the water content dip below 30%.

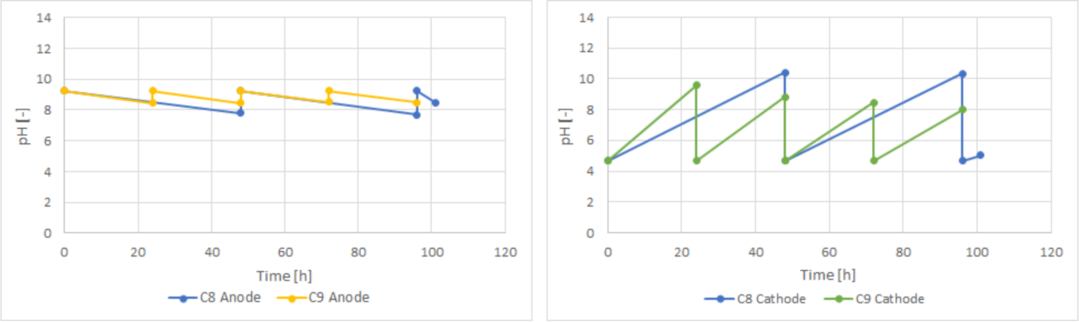


(a) (b)

Figure 5.8: *Moisture content of clay poultices for samples C8 (a) and C9 (b).*

The pH of the poultices is presented in Figure 5.9. The initial pH value of the poultices are quite different, as the purpose of the anode clay is to buffer acidification. The initial anode pH is 9.25 and the initial cathode pH is 4.68. The two samples show a similar behaviour behaviour of the pH when considering anodes and cathodes separately. The longer a poultice is used, the more its pH changes from its starting value. This is explained by the accumulation of H^+ or OH^- ions as a result of the ED treatment (Section 2.2.1). Only one pH value is acidic, and that is the cathode poultice that is used for treatment only for a few hours. Due to the short treatment time, the hydrogen ions have not been gathering around the cathode in a large enough amount to raise the pH.

The accumulation of Na^+ and Cl^- ions within each poultice is presented in Figure 5.10. The



(a) (b)

Figure 5.9: *pH of clay poultices used during ED treatment of samples C8 and C9. The graphs are divided into the anode poultices (a), and the cathode poultices (b).*

$NaCl$ content of the sample when initially saturated is also marked on the graph. The final $NaCl$ content of the samples were 6mg for C8 and 2mg for C9, therefore the accumulated salt content of the poultices should reflect the initial $NaCl$ content.

While the poultices of sample C9 contains close to the amount of salt that was removed from the sample, this is not the case for the poultices of sample C8. The total salt content gathered by the poultices is just below 500mg, but there was over 700mg at the start of the treatment. Based on Table 5.5, the sample is desalinated, which is backed up by the conductivity measurements presented in Table 5.4. The discrepancy between the measurements of the poultice clays and the stone sample could be explained by a loss of material during the analysis process.

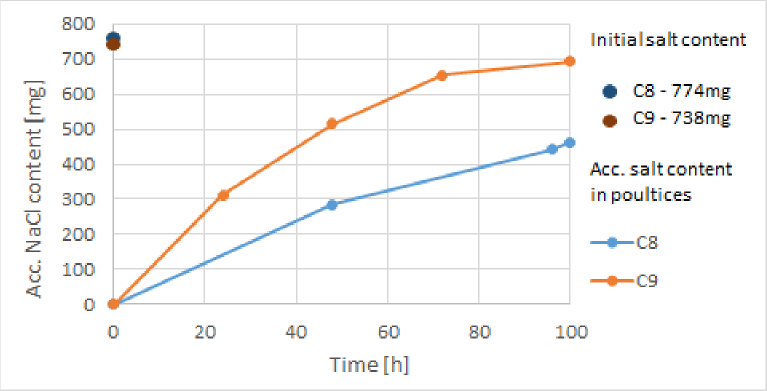


Figure 5.10: *Accumulating $NaCl$ content within clay poultices from ED treatment of samples C8 and C9.*

Measuring the salt content of the clay used to be the only non-destructive way to monitor ED treatment. As is clear in Figure 5.10, this might not be the most accurate method. In the case of these samples, C8 would be treated further based on this data, which would increase the likelihood of side effects (Section 2.1.3).

For both samples, the first poultice changed contain ca. 300mg $NaCl$ after treatment, but this happens after 24h for C9 and after 48h for C8. A similar increase is seen in poultice 2, but again, there is 24h between the C9 poultices and there is 48h between the C8 poultices. This could indicate that there is a ”maximum” uptake of salt into the clay (at 300mg), something that should be investigated further, as there otherwise is no differences between the samples but the timing of clay changes. From this data it is clear that the rate of removal of salt wanes over time, no matter how often the poultices are changed. The efficacy of the ED treatment will be further investigated in Chapter 7.

5.3.3 Changes to clay properties during ED treatment

Throughout the treatment the properties of the clay change. As was presented in Section 2.2.1, when an electrical current is applied to a system containing water, one of the effects will be electro-osmosis. This drives water towards the cathode electrode, away from the anode electrode. However, no drastic difference in water content between anode and cathode poultice is seen in the data presented in the previous section.

Even though the data shows a small difference in water content before and after treatment, the observations made during treatment are that the cathode becomes overly saturated with water. The water leaks out through the gap of the cling film where the cathode electrode is inserted into the system. The added water affects the electrode’s ability to stay in place, the resistance in the system increases and peaks can be seen in the data for potential difference.

Another effect seen during treatment is that the weight of the crocodile clips seem to be enough to pull the electrodes out of the clay at times. Tape or rubber bands can be used to keep the electrodes in place, but it can be a constant struggle, due to the change in consistency of the poultice during the ED treatment.

Because this experiment includes the samples being disconnected from the ED treatment and handled for impedance measurements, any problems with the connections of the electrodes are noticed early, and the poultices can be given a squeeze to ensure the connection. This also improves the connection throughout the ED treatment and the peaks in voltage are therefore not as common as if the samples were left untouched.

5.3.4 Effects of clay changes

It could be supposed that the clay could ”fill up” to a maximum salt content. If this was the case, it would be more efficient and drag out more salt if there were less salt in the poultice, and a more frequent exchange of clay would be beneficial. However, based on these results, changing the clay only adds extra work, and results in a lower water content of the sample. This is as a result of electroosmosis, which takes place in preference to salt movement in the right circumstances (Section 2.2.1). Each time new clay is introduced, water is added to the system and electroosmosis is the main process within the system for a while. Rather than changing clay often, it should be done as little as possible to keep the sample at as high moisture level as possible during treatment to ensure a good electrical connection throughout the system.

There is also the question of connection to the electrodes. When the systems are introduced an electrical current and the electroosmosis drive water towards the cathode side it dissolves the connection between this electrode and the clay. When left in place, the clay and electrode seems to have a more stable connection. Keeping in mind that if left unattended the electrode can fall off due to mechanical stresses from the crocodile clips that are used for connecting the electrodes to the power supply. Electrodes have, in this study, been known to detach from the clay for the following reasons: Too much water in the clay; Not enough water in the clay; Gravity (Section 5.3.3). It is therefore important to not only consider the duration of each poultice pair during treatment, but also it is vital to ensure a strong connection between clay and electrodes at all time, through any inventive means available to the user. This user has been working successfully with tape but might in the future consider rubber bands.

Based on the data from these experiments no advantage can be seen in exchanging the clay more often. Instead, changing clay less often seems to reduce moisture removal. The purpose of changing clay often in experiments prior to this thesis [e.g. Andersson, 2017b] was to investigate the amount of salt removed during a given time. However it will be shown in Chapter 7, that impedance will be able to do this instead. Therefore in the later experiments the clay was not changed in order to contain the amount of variables affecting the results.

5.4 Summation of chapter

Based on the literature presented in Section 2.3.3 it should be possible to monitor the treatment of salt removal using impedance measurements of the sample. This chapter contains an electrode set-up developed for this purpose. The maximum electrical current that can be applied during ED treatment has been investigated, and early trials have suggested that impedance changes drastically between a sample that is saturated with salt and that is desalinated.

The previous method for monitoring the amount of salt removed from a sample, analysing the poultices, has also been considered. The conclusion is that it would be better for the treatment and the sample if a different method could be devised to prevent potential difficulties during treatment and damage to the sample.

6 Investigation of variables for impedance

6.1 Introduction

In order for electro-desalination (ED) to be a useful tool in stone conservation, the operator needs to understand when the treatment is 'complete'. As stated in Section 2.3.3, impedance could potentially be used as a tool to monitor the progress of desalinisation. This chapter contains an investigation of variables for impedance measurements, and a discussion based on these results on how impedance could be used to monitor the electro-desalination treatment.

As stated in Chapter 2, Lehmann and Krüger [2014] showed that it is possible to detect movement of water and salt in porous materials using impedance. They concluded that further studies are required to determine the relations between different variables in and around the system, such as porosity, moisture saturation, salt content, temperature and humidity. In his thesis, Lehmann [2018] demonstrates the importance of moisture, pore size distribution and temperature in influencing the bulk conductivity of porous materials. Lehmann's study principally focused on the monitoring of water movement through porous materials, with only a minor investigation of salt content.

To address this gap, this chapter investigates the influence of sample porosity, moisture content and salt content on impedance measurements, using the electrode set-up presented in Section 5.1. Neither temperature or humidity have been investigated further in this study, as all experiments are conducted in lab settings, where neither of these changed drastically during the year, and as such, are not expected to be the main variables for these measurements.

First the experimental design for each variable (sample porosity, moisture content and salt content) is presented, followed by a section dedicated to results for each variable in turn. The discussion of these results are then presented. The purpose of this chapter is to investigate if impedance is a viable tool for monitoring salt removal techniques.

6.2 Experimental design

The experimental setup developed in Chapter 5 is used to investigate the influence of individual parameters. Two types of stone were examined: Claschach Sandstone and Stanton Moor Sandstone (Section 3.2). Throughout the experiment, the impedance is measured for the single frequency 1kHz, because it functions as an approximation of the sample's resistance as explained in Section 2.3.3.

6.2.1 Variability in sample porosity

As in all natural materials the samples used in this study contained inherent variability. The Clashach sandstone samples used are cut from several blocks while Stanton Moor was cut from one block.

Some of the Clashach Sandstone samples were massive with no visible features. However, about a third of the samples contained fine scale (millimetres-thick) laminations some of which were stained with iron oxides. The samples were assigned visually by an experienced geologist (Dr. Zoe Shipton), and sorted into three groups: high iron band content, medium and low. They were then tested in the potentiostat when dry and when saturated with ultra-pure de-ionised water in order to investigate the porosity's influence on impedance measurements.

Because of the variability within the Clashach Sandstone samples, a separate results section (Section 6.3.1) will address the possibilities for impacts in impedance based on the iron bands. Section 6.3.2 addresses the variability in sample porosity.

The porosity of all the samples were measured using the Archimedes method described in Section 3.2.1, the results of which are presented in Section 4. The samples have then been tested for impedance while dry and wet. The relation between porosity and impedance is presented in the results section of this chapter.

6.2.2 Procedure for generating samples with known water saturation

The first set of data concerning moisture saturation uses the same measurements of dry and wet samples used for comparing porosity and impedance. The second set of data concerns samples with varying levels of moisture content.

This was achieved by saturating six samples (C7-C12) with DI water. The samples were weighed before and after saturation, and thus the total amount of water in each 100% saturated sample was measured. The starting impedance was also measured and a drying process ensued. The samples were set out at room temperature and left to dry. Each sample was weighed in 5min intervals, and after losing 1g of mass (water) it was placed in a sealed box on its own in order to let it homogenise. This step prevented formation of a drying front which could affect measurements. After 4h or over night, the samples were weighed again to check that the water content had not changed, and the samples measured for impedance. This procedure was repeated until the samples were completely dry.

As presented in Section 2.1.1, the development of a drying front within the samples would affect the impedance measurements. Instead of a continuous liquid connection throughout the pore structure, the pores would be partially water saturated and partially air filled, therefore increasing the measured impedance of the stone. This is the reasoning behind the homogenisation time of the samples, where any drying front can equalise with the surrounding pores. There was however no control on whether this was achieved. Therefore variations in the measurements can stem from a lack of continuous water connection within the pores.

In order to more easily compare samples with varying mass and porosity the saturation level of the samples are calculated using the following equation, where m_t is the mass of the sample at the time of interest, m_{dry} is the sample mass when dry and m_{wet} is the sample mass at 100% DI water saturation.

$$SL_t = \frac{m_t - m_{dry}}{m_{wet} - m_{dry}} * 100 \tag{13}$$

The measurement increments were based on loss of weight from the samples. The data points are therefore gathered at varying saturation levels, as this is dependent on each sample's porosity.

6.2.3 Salt concentration

The final variable that is investigated is salt content. As is well known salt influences electrical measurements. In this study the focus is on Sodium Chloride. This section explains the method of investigating the influence of salt concentration on impedance measurements.

First, three of the above samples (C7-C9) were saturated with $1mNaCl$ solution and measured for impedance. They were then desalinated using ED treatment and tested again on completion of the treatment. User experience of the desalination process was used to dictate when the treatment was thought to be complete. The initial salt content was calculated using the weight of absorbed salt solution, and the final salt content measured using IC/ICP.

In order to investigate the impact of varying salt concentrations, more Clashach Sandstone samples were vacuum saturated with $NaCl$ solution, with four different concentrations presented in Table 6.1 (repeated from Section 3.6.2).

Table 6.1: *Tested concentrations of Sodium Chloride*

Concentration	Molality (m) [mol/kg]	Weight percent [wt%]
Accepted	0.2	0.03
Contested	0.5	0.8
Unaccepted	1.0	0.16
Extreme	1.5	0.24

These concentrations range from an accepted level ($0.2m$) that is considered to be safe, to an extreme level ($1.5m$) which is expected to be highly damaging to building materials. After the samples are saturated they are measured for impedance in the potentiostat. The salt content of the samples are again based on the absorbed weight of salt solution for each sample.

6.3 Results

6.3.1 Variability between samples

The Clashach samples were divided into three categories; low, medium and high visual iron band content, as based on visual observations of iron banding within the samples. A photo of the samples after the grouping can be seen in Figure 6.1.

Figure 6.1: *Clashach samples divided into sub-groups based on their visual assessment of the amount of iron-stained bands*

The samples porosity are shown in Figure 6.2, and their impedance while dry and wet are presented in Figure 6.3.

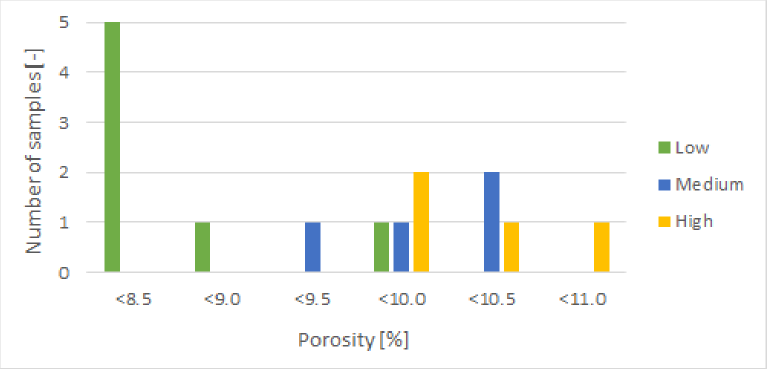
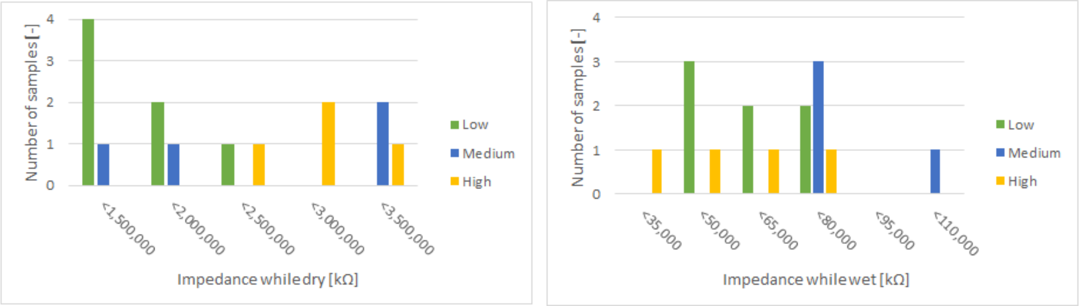


Figure 6.2: *Porosity of the sub groups of Clashach samples; with low, medium or high visual appearance of iron bands*

The samples with lower porosity have a lower prevalence of iron bands. Porosity is explored further as a separate variable in the next section.

When the samples are dry, there is a separation between the low and high iron content samples, but no relationship is seen for the samples with medium iron concentration. It was easier to differentiate low iron content samples from the other groups, and the difference for medium and high iron content is purely visual. It is therefore possible that the separation between the groups are coincidental, as the pattern is also not duplicated for when the samples are wet. As no link can be established between visual appearance and impedance measurements t, the iron



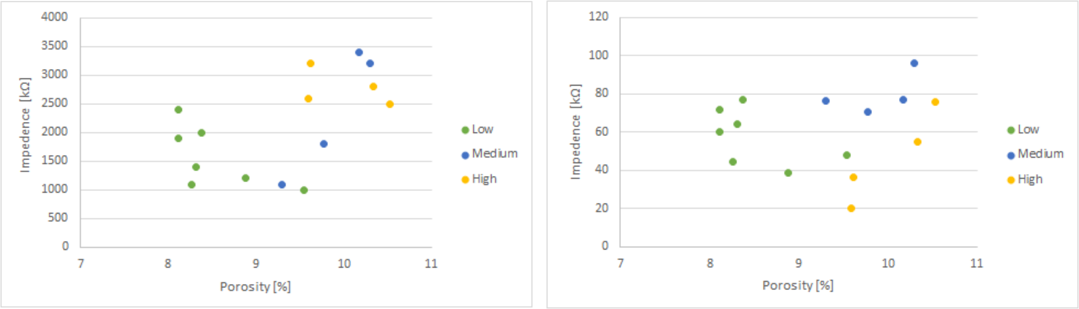
(a) *Dry* **(b)** *100% Saturated with DI-water*

Figure 6.3: *The impedance of samples while dry (a) and wet (b), sorted into categories based on the visual appearance of iron bands*

band content is not considered further as a potential variable in this study.

6.3.2 Porosity

As discussed in Section 2.3.3, when electricity moves within porous inert material, it tends to move through the pore system, rather than the stone matrix/grains. It is therefore of interest to compare the impedance measurements to the sample's porosity. The results are presented in Figure 6.4a for dry samples, and in Figure 6.4b for samples 100% saturated with DI water.



(a) *Dry samples* **(b)** *100% saturated samples, DI water*

Figure 6.4: *Impedance [kΩ] measured on 15 samples (C6-C20) compared to the sample's porosity when they are (a) dry and (b) 100% water saturated. The grouping of the samples are as in the previous section based on visual iron staining. Note the different scales on the y-axis.*

The dry samples have an average impedance of 2100 kΩ compared to the wet samples which average at 60 kΩ. This confirms that it is the liquid in the pores that conducts electricity, rather than the grains of the rock. However no relation between impedance and porosity is seen here, for either dry or wet samples.

To investigate the impact of porosity further, 10 samples of Stanton Moor Sandstone were investigated. Stanton Moor has a similar composition to Clashach but generally has a higher porosity (Section 3.2). The Stanton Moor samples, numbered S1-S10, were saturated 100%

with DI water and the impedance was measured. The results of which are presented in Figure 6.5 together with data from 24 Clashach samples that were also saturated 100% with DI water (C7-C20, C30-C39). The average porosity of the Stanton Moor samples is 13% and the average for the Clashach samples is 11%.

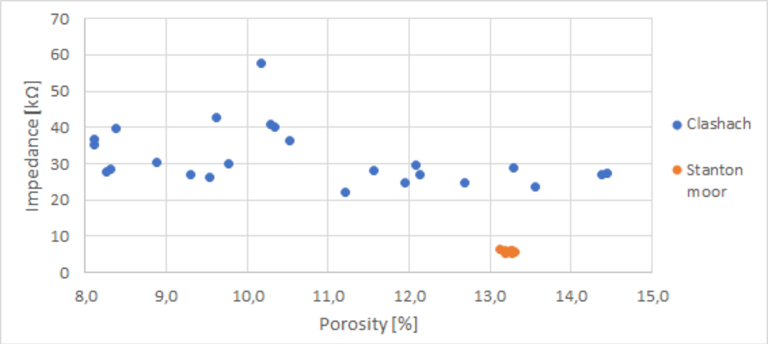


Figure 6.5: *Impedance and porosity for 24 Clashach samples and 10 Stanton Moor samples*

The Clashach samples have an average impedance of 36kΩ, while the Stanton Moor samples have an average impedance 6kΩ. Apart from the difference in impedance, there is also a larger variability for the data concerning the Clashach samples than the Stanton Moor samples. In order to check the variability of this data, in Figure 6.6 the impedance for each sample is divided by the mean of the entire population, normalising the data.

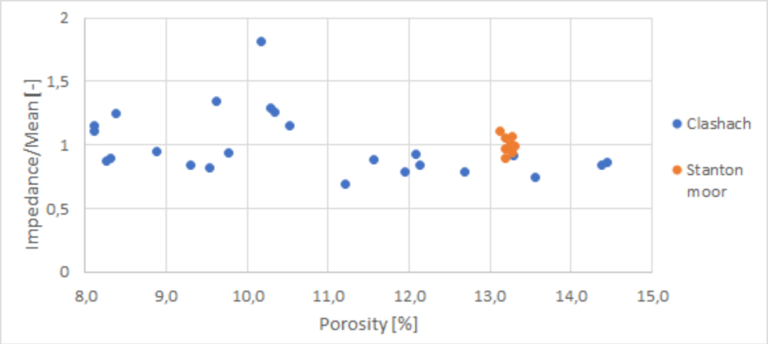


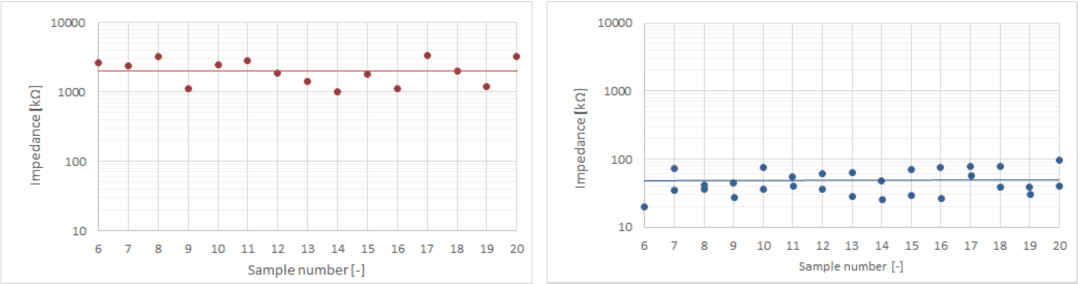
Figure 6.6: *Normalised impedance over the population mean for Clashach and Stanton Moor samples*

There seems to be no correlation between porosity and impedance for either type of sandstone. From this dataset porosity alone is not the deciding factor for impedance values at 100% saturation. It is more likely that there are other factors that determine the impedance. It is known from Lehmann [2018] that the effective porosity influences the impedance, as this speaks to the connected pore structure, as does pore size distribution. Neither of these properties have been measured during this study.

Sandstone is a naturally heterogeneous material, and it seems from these data that there is a higher degree of heterogeneity on the Clashach than the Stanton Moor.The larger variability within the Clashach population could also be due to the fact that Clashach samples were cut from different blocks of stone whereas the Stanton moor samples are all cut from the same block, just a few centimetres apart from each other.

6.3.3 Impact of moisture content on Clashach samples

To investigate the effect of water saturation on impedance, data for multiple samples (C6-C20) are presented in Figure 6.7a for dry samples and Figure 6.7b for 100% water saturated samples. The samples are ordered by sample number, and all samples were measured twice while wet, apart from C6, that was measured once. With one exception (sample C8) all the lower values were measured the second time, in January, rather than the first time in September the year prior. The reruns were conducted to establish the range of variation between measurements of the same sample, as variations are expected, explained further in Section 2.3.3. Re-runs were not conducted for dry samples as it proved difficult to get accurate readings of the samples in this condition. This is also explained in Section 2.3.3.



(a) *Dry samples* **(b)** *100% saturated samples, DI water*

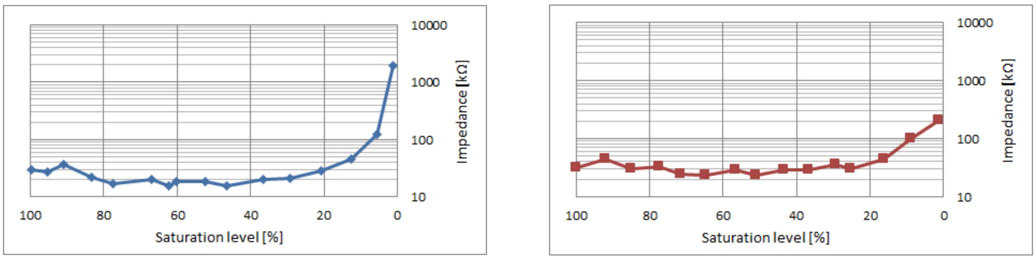
Figure 6.7: *Impedance values for dry (a) and 100% water saturated (b) samples with the mean presented as a straight line. The x-axis in these cases is the sample number, most of which have been tested twice while wet (indicated by dots on a vertical line).*

When the samples are wet, the impedance is between 10 and 100kΩ and the standard deviation of the measurements are at 18kΩ. Repeat measurements of a single sample show variability, for instance sample C7 was measured three times with an impedance of 35kΩ, 72kΩ and 78kΩ.

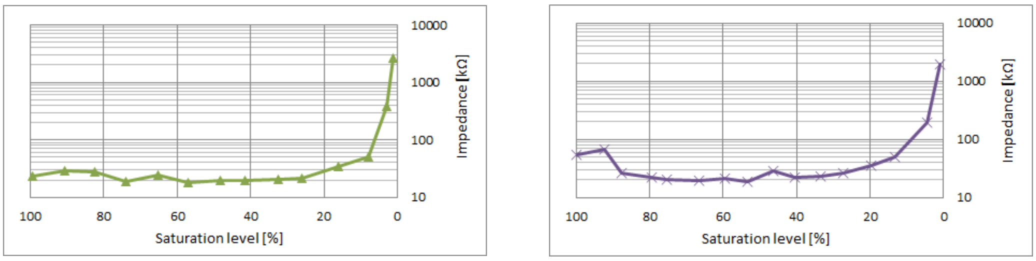
When the samples are dry, impedance values are above 1000kΩ with a standard deviation of 800kΩ. This high variability is due to the high values of impedance (Section 3.4). Repeat measurements when dry did not return reliable values and were discarded in accordance with the quality assessment presented in the same section.

These graphs show a clear difference in magnitude of impedance for dry and wet samples, as expected. These variations, are explained further in Section 6.4.1 and does not influence the overall conclusion that impedance is affected by moisture content within the pore system.

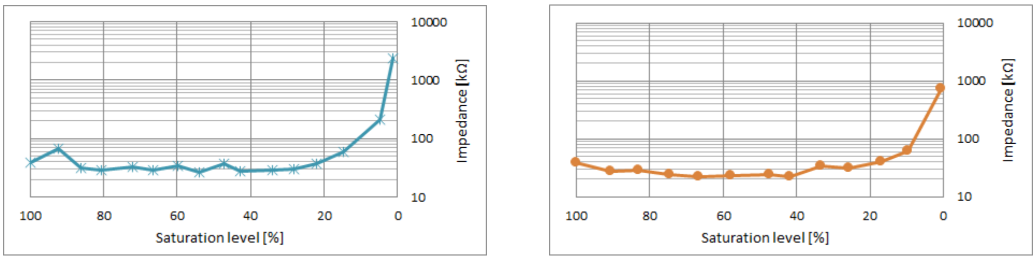
In order to investigate the correlation between impedance and moisture content, a second experiment was conducted. Six samples (C7-C12) were saturated with DI-water and left to dry in intervals. At each interval the impedance was measured. The experiment took place over a week, with every sample conditioned and analysed under the same environmental conditions of temperature and RH in order to minimise any further extraneous variables. The results are shown in Figure 6.8, the y-axis is logarithmic.



(a) *C7* **(b)** *C8*



(c) *C9* **(d)** *C10*



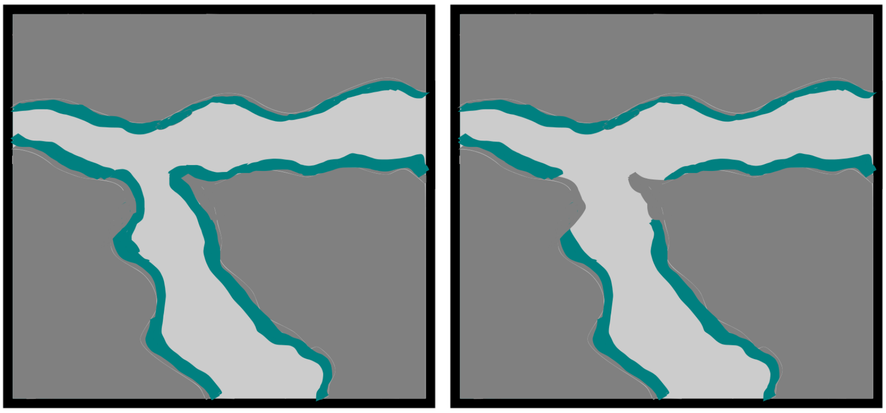
(e) *C11* **(f)** *C12*

Figure 6.8: *Impedance for samples C7-C12 at varying water saturation levels while drying. The water saturation is represented on the x-axis, where 100% represents the maximum amount of water possible to be retained within the sample. The y-axis represents the measured impedance at 1kHz. Note that the y-axis is logarithmic. Measurements started at 100% saturation and samples were air dried to constant mass.*

All six samples show the same power law relationship between moisture and impedance. Impedance remains stable between 10 and 100kΩ until about 20% saturation. At saturation lower than 15% the impedance rapidly increases, reaching as high as 2700kΩ in sample C9.

The increase in impedance follows an inverse exponential relationship. This can be explained by recalling the two stages of drying described in Section 2.1.1, illustrated in Figure 6.9.

In Stage I, the constant rate drying phase, a liquid film on the pore walls connects the inner pore structure and the surface of evaporation. This creates a continuous electrical connection



(a) *Stage I* **(b)** *Stage II*

Figure 6.9: *Stage I (a) and II (b) of drying of porous media. Stage I has a continuous connection of a liquid film throughout the pores, in Stage II, this liquid film is disconnected.*

for the measurements taken during drying phase I. In Stage II, the falling rate drying phase, the surface tension of the liquid films in the pores decrease until some of the film layers breaks apart (Figure 2.2). At this point the electrical resistance will increase as the electrical current has fewer liquid paths to move through. Eventually the electrical current has to move through the phase change(s) of air to water which will increase the impedance further.

The impedance measurements of above 15-20% saturation are all within the previously established range for wet samples of 10 and 100kΩ. Because of the stability in results it is likely that this represents Stage I drying where a connective liquid film layer throughout the samples create a stable connection for the electrical current. The measurements below 15% saturation are likely to illustrate stage II drying as there is a sharp increase in impedance, indicating a loss of electrical and therefore also liquid connection through the pore structure.

All values including 0 and 100% saturation for all six samples fall within the ranges displayed in Figure 6.7. The variability in the measurements will be further discussed in Section 6.4.1.

The final value of impedance varies from 210kΩ for sample C8 to 2700kΩ for sample C9. This range is lower than the dry samples in Figure 6.7, likely due to residual moisture in some of the samples as air drying in room temperature is not as efficient as drying samples in an oven at 105°C.

The data presented in this section demonstrates that as long as the moisture saturation is above 20%, the variations seen in impedance measurements are not dependent on the moisture content.

6.3.4 Salt

The previous experiments investigated the effect of varying moisture saturation using DI water. Introducing salt to the system should result in a decrease in bulk sample impedance. To check the influence of salt in the pore fluid, three samples were measured (i) dry, (ii) wet with DI water, and (iii) wet with $1mNaCl$. In Figure 6.10) the first two data points are when the samples are dry, the next two when the same samples are saturated with DI water (using the technique presented in Section 3.2.3), and the fifth point when the samples are saturated with $1m\ NaCl$. The final points for each sample are impedance after completed desalination treatment.

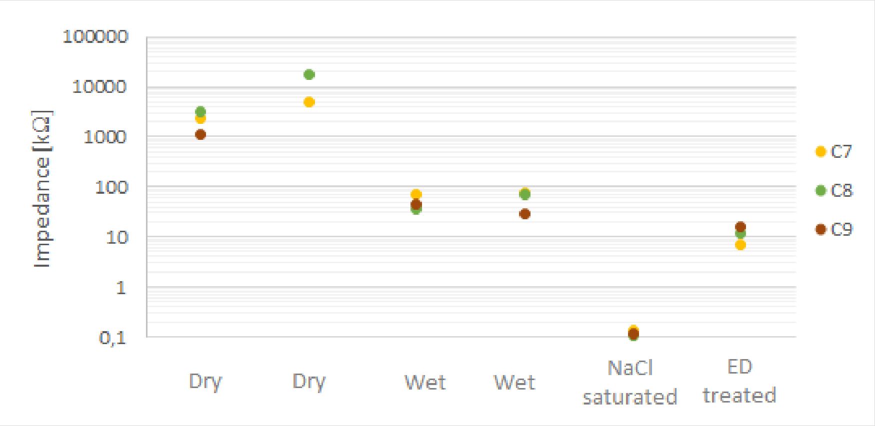


Figure 6.10: *Impedance measurements for samples C7, C8 and C9 when dry, 100% saturated with DI water (wet), saturated with 1m NaCl and after ED treatment. The y-axis is logarithmic.*

There is a significant difference between impedance when samples are saturated with a salt solution compared to DI water and again to the dry samples. The data from the dry and 100% DI water saturated samples are included in the analysis in Section 6.3.3. These three samples show a typical level of variability as seen in Section 6.3.1).

The 100% salt-saturated samples have an average impedance of 0.145kΩ, over two orders of magnitude lower than samples saturated 100% with DI water. Once the samples are desalinated with ED treatment, they have a similar impedance to when they were saturated with DI water (10 to 100kΩ). This implies that ED has removed almost all of the salt. In order to prove that this is the case, the salt content of the samples was measured after treatment using IC/ICP (Section 3.5.4). Table 6.2 shows the salt concentrations within samples prior to ED (calculated according to Section 3.6.2) and after ED, together with the total salt content reduction and the final moisture saturation.

Table 6.2: *Salt concentration for C7-C9, before and after treatment*

	Porosity [%]	Iron bands (Yes/No)	NaCl content before ED [mg]	NaCl content after ED [mg]	Total salt reduction [%]	Final moisture saturation [%]
C7	8.1	No	725	6	99	57
C8	9.6	Yes	829	6	99	67
C9	8.3	No	747	2	100	31

All samples showed a reduction in total salt concentration between 99% and 100% as a result of ED treatment. This means that the likelihood of residual salt crystallisation related problems are minimal.

The moisture saturation in the samples decrease during the ED treatment. None of the samples have a moisture saturation lower than 20%: the point at which the moisture content of the samples starts to influence the replicability of the impedance measurements (Section 6.3.3). This gives confidence in the impedance values that suggest salt is being removed, which is confirmed by the IC/ICP data.

There is a difference in final moisture saturation values, whereby C7 and C8 have around 60% saturation and C9 at only 30%. This difference can be explained by how often the clay in the electrode compartments was exchanged during the treatment. The first two samples had clay exchanged every 48h, whereas C9 had the clay exchanged every 24h. This was in order to investigate the effects of clay exchange frequency. It is clear from this data that applying new clay leads to an increase in water moving from the stone sample into the clay. Exchanging clay more often therefore leads to a larger reduction of water within the samples. This should be avoided in order to provide a good electrical connection throughout the sample, and therefore easing removal of unwanted salt ions.

As long as the samples have a moisture saturation greater than 20%, then the main variable that influences impedance measurements in this study is the salt content.

6.3.5 Varying salt concentrations

The difference in impedance between samples saturated with $1mNaCl$ solution and DI water has been established. In order to investigate the influence of varying salt concentrations on the impedance measurements, three more salt solutions were made in accordance with methods in Section 3.6.2. The chosen concentrations, presented in Table 6.1 are intended to represent: (i) a concentration which would not create damage in the samples ($0.2m$), (ii) one that might result in damage ($0.5m$), (iii) one that will ($1m$), and (iv) one that would generate substantial damage ($1.5m$), according to Önorm [1999].

Five Clashach Sandstone samples were saturated with each solution. The impedance measurements for these samples together with data for 10 samples saturated with $1m$ are presented in Figure 6.11. The salt content of each sample has been calculated based on the amount of salt solution absorbed during saturation. The spread of salt content values along the x-axis is due to the variation of porosity between the samples.

Figure 6.11 shows a power-law fit relating salt content and impedance measurements. The correlation shows that higher salt content is indicated by lower impedance. Based on the shape of the curve, it could be conceived that there will be a value of salt concentration above which the impedance will no longer decrease.

All samples have an impedance of less than 500Ω when saturated with salt solution. When

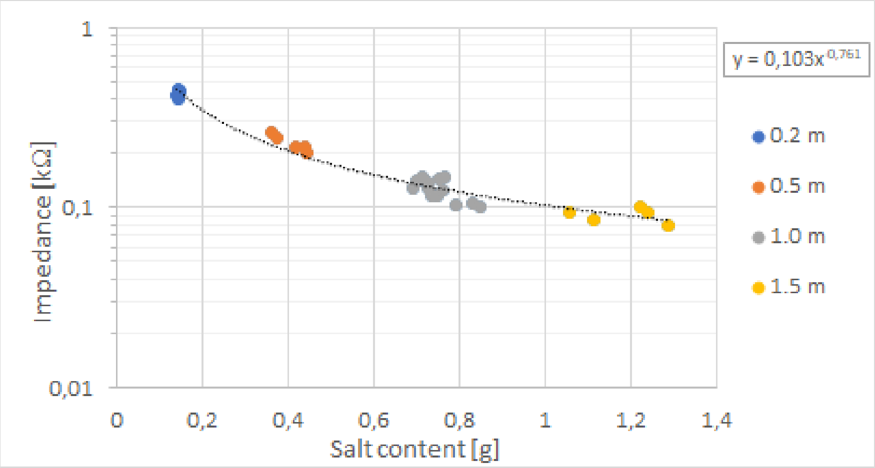


Figure 6.11: *Impedance values for samples 100% saturated with $NaCl$, in four different concentrations, 0.2m, 0.5m, 1m, 1.5m*

the samples are saturated with DI water they have an impedance of at least 10kΩ. In order to investigate at which point salt can no longer be detected using impedance, the measurements from the desalinated samples C7-C9 are added to the data from the previous figure. In order for the data to be comparable to other studies, the salt content is presented as grams of salt per grams of dry sample. The results are shown in Figure 6.12.

The salt concentrations of samples C7-C9 after ED contain less than 0.01g $NaCl$, measured using IC/ICP. The samples saturated with 0.2$mNaCl$ contain ca. 0.14g of salt based on calculations of sample weight change after salt solution saturation. The 0.2m samples contain more than 15 times the amount of salt than the desalinated samples.

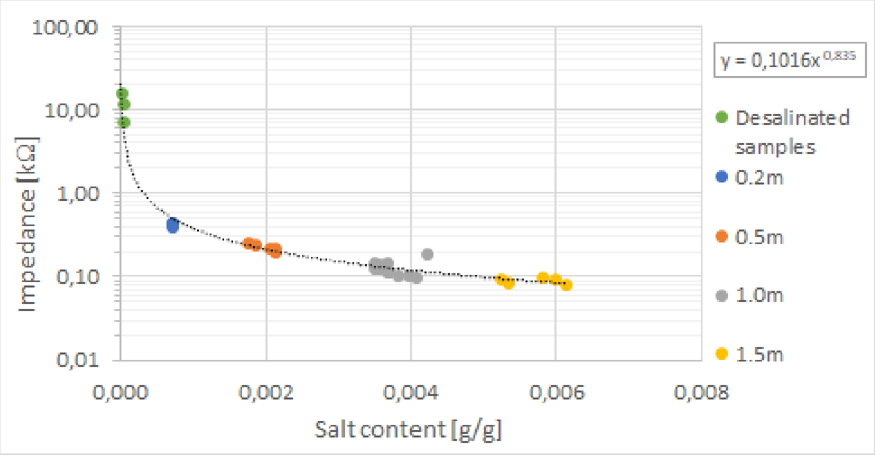


Figure 6.12: *Impedance of samples with varying salt concentrations, including desalinated samples (C7-C9) containing <0.01g$NaCl$.*

When the data are presented on a log scale (Figure 6.13), the trend line describes a power law between salt content and impedance. A power law is indicative of a complex system, where there is a parallel scaling of impedance and salt content. As there are very few outliers from the trend line, this could be a useful predictive relationship between impedance and salt content.

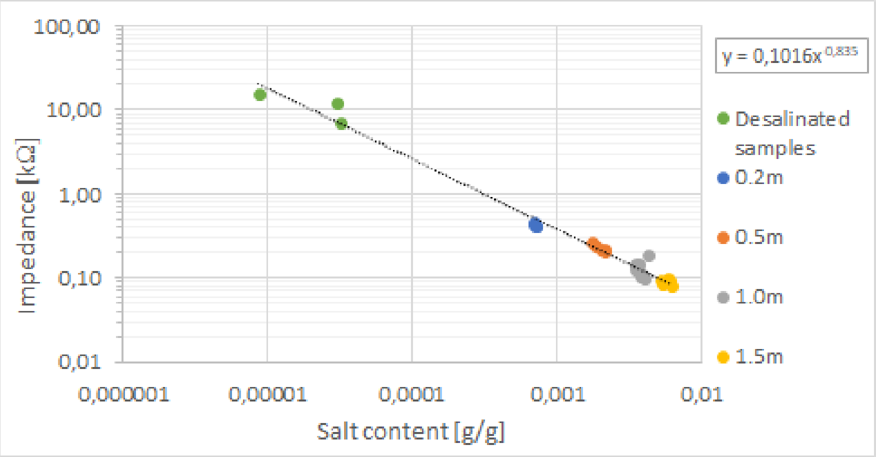


Figure 6.13: *The impedance and salt content of samples with varying salt concentration, where both the y and x-axis is logarithmic.*

The trend line for Figure 6.12 is very similar to that of Figure 6.11. This demonstrates a clear connection between salt content and impedance measurements between 0-1.5m. As mentioned above, based on the asymptotic behaviour of the trend lines, there could possibly be a point where impedance can no longer be used to identify an increase in salt content.

If a different material were used for the same measurements it would result in a similar trend line as the main factors influencing these measurements is the salt content (Section 6.3.4). Considering Stanton Moor as an example, the intercept on the y-axis would be lower, as the samples saturated with DI water have a lower average impedance than the Clashach samples (Section 6.5). As discussed in Section 6.3.2 Stanton Moor is presumed to have a better interconnection between the pores compared to Clashach. This would ease the electrical conduction for samples saturated with salt solution as well, resulting in lower impedance values.

There is a clear correlation between salt content and impedance shown by a mathematical curve. Also, the drastic increase in impedance when the salt content is reduced below 0.1g provides a direct indicator that the samples are desalinated.

This leads to two conclusions from this chapter: 1) it should be possible to relate a certain impedance value to an estimation of salt content, and 2) if an alarm is set at fx. 2 kΩ that switches off desalination, the sample will be protected as it is either dried out or it is desalinated.

6.4 Discussion

Here the results for the different variables investigated for impedance measurements are discussed. First each sub section for sample variability, porosity, moisture content and salt. Then a caveat to these results is presented, and a deeper discussion about these variables ensue. The conclusion is that impedance shows promise for monitoring desalination treatments. Future studies will be addressed in Section 8.

6.4.1 Variability in measurements

Throughout this study, quality checks have been carried out on the data obtained in the potentiostat in accordance with the criteria outlined in Section 3.4. If the measurements produced include large amounts of noise, change over time or provide negative values, they are disregarded.

Obtaining valid measurements proved especially difficult when it came to dry samples. The dry samples also have a higher variance of impedance than wet samples when valid measurements were made. This is partly attributed to the sensitivity of the potentiostat: the variability in measurements becomes larger at higher values of resistance, further explained in Section 3.4. The higher resistance in dry samples are due to the lack of conducting material within the pore network. Both the stone matrix and the air within the pores have a poor conductivity and as such prevents the electrical current from passing through the system, further explained in 2.3.3.

Lehmann [2018] demonstrated the influence of relative humidity and temperature on impedance measurements. The influence of relative humidity can be disregarded in this study as the samples and their entire systems of clay and electrodes are wrapped in cling film and as such should not respond to changes in the humidity of the surroundings. The variability in measurements resulting from temperature changes is attributed to the resulting temperature of the solution within the stone matrix. As such, the variations are larger at lower moisture contents. As the lab is temperature controlled at 20±1°C no variations in impedance is expected from the ambient temperature.

The variations in the impedance values for 100% saturated samples in Figure 6.7 are larger than the differences seen in [Lehmann, 2018]. It is therefore assumed that the temperature is not responsible for these measured variations. The variations seen in the partly saturated samples of Figure 6.8 are largely within the range of 5kΩ and so most of the differences in the data over 20% saturation could be explained by variations in temperature. A time series of temperature measurements taken every 10s in the lab over 6h in march 2021 show an average of 21.7°C, with a variation of 0.05°C. As this indicates a steady temperature in the labs, this is unlikely the source of the variations in impedance measurements. However, the samples might be experience heating as a consequence of the application of electrical current. The amount of heating would be a function of the impedance of the sample.

The variability in measurements can be attributed to inherent measurement error, assembly of the samples treatment system or changes within the samples. The measurement errors for the potentiostat are very small, as discussed in Section 3.4 but the sample assembly can be very influential as described in Section 3.3. It is essential for the measurements reliability to ensure a good connection between poultice and stone. Changes in the samples is referring to change in moisture or salt, variables that are measured and considered in this study.

6.4.2 Results

The investigation into how sample variability (in the form of visible iron bands) affects the impedance measurements has shown that it does not in the case of dry or wet samples. However, a correlation between the samples' porosity and the amount of visual iron bands was noticed. Lower iron band content indicates a lower porosity.

From the results shown in Figure 6.4, there is no correlation between porosity and impedance for dry or wet Clashach Sandstone samples. In comparing two different types of sandstone (Figure 6.5), the impedance values were higher in the lower porosity stone (Clashach) than the higher porosity stone (Stanton Moor). As Lehman [2018] found that the main variable that determines samples absolute impedance value is the specific surface area. This is likely also the case for the samples in this study. If so, the lower impedance for Stanton Moor would indicate a larger surface area. This can be collaborated by the measurements from Graham [2016] where Stanton Moor has a greater pore size distribution and a higher proportion of smaller sized pores than Clashach. Many small pores results in a greater specific surface area then fewer large pores. If this is the reason behind the impedance measurements, it would explain why no impact is seen for porosity on only Clashach samples, but a correlation can be seen when comparing two different types of stone. As porosity is the only value that has been measured in this study, this can not be confirmed here.

The impedance of the dry Clashach Sandstone samples is very high, meaning that the overall sample resistance is high but variable, even between repeat testing of a single sample. As explained in Section 2.3.3, for each measurement, the current can take many different paths through porous media. When all of the paths available are highly resistant, the struggle for the electrical current to get through will come up as more variability in the measurements. Despite the inconsistency within the populations, it is quite clear that the samples' impedance when dry is at least 2 magnitudes higher than when saturated with DI water.

Two stages of drying can be identified. Stage I where the impedance is relatively constant around 40kΩ, until ca. 20% saturation level where impedance increases exponentially. Values between 100 and 1000kΩ seems to indicate drying stage II, where the connection of water throughout the sample is likely disrupted. It is worth considering that the crucial point is not the saturation level itself, but rather the connection of water through the sample's pore structure. A separate study into this will have to be made to investigate this hypothesis further.

Salt saturated samples show a distinct difference in impedance from samples saturated with DI water in Figure 6.10. All measurement of impedance from samples saturated with salt concentrations of $0.2m$ or more were below 500Ω, shown in Figure 6.11. This is two magnitudes less than DI water saturated samples.

As shown in Figure 6.10, samples that have been desalinated have an impedance of ca. 10kΩ.

Combining this with the data from the moisture experiments, it could be argued that as long as a sample's water saturation is above 20%, and the impedance measured is lower than 10kΩ, it is very likely they contain some amount of salts, in accordance with the findings of Lehmann [2018]. Once 10kΩ is reached, the sample is likely desalinated. Even though this can be further investigated in detail, having an estimated "finish line" of impedance for desalination treatment is already very useful for conservators.

6.4.3 Analysis

It is important to point out that the specific values for impedance can only be concluded to be related to these samples, at room temperature. A difference in stone type, stone size, salt type, salt concentration or environment could alter these numbers significantly (Section 2.3.3).

Different stone types have different parameters such as porosity, connectivity of pore structure and mineral composition. It is clear from these data that despite a similar composition and porosity, Clashach sandstone and Stanton Moor sandstone vary in impedance. This would also be the case for other types of materials. Based on these results it is clear that porosity is not a major factor for impedance, in concurrence with the results of Lehmann [2018].

This study is only focused on materials which have inert matrices, and as such the electrical current is only conducted within the pore structure. Other materials that contain clay or metals might provide other pathways for the electrical current. This would in turn affect the impedance measurements. For further understanding of this concept, further studies are required.

The measured impedance is also dependent on the distance between electrodes (Section 2.3.3, which in this scenario, relates to the length of the samples. A different size sample of the same rock should yield a different, larger, impedance range. This is because the electrical current has a longer distance to cover, which increases the electrical resistance of a system.

A solution's ability to conduct electricity is dependent on the salt ions it contains. As ions carry the current within the solution, the theoretical ionic mobility of each ion will determine the efficiency of desalination. Heavy or large ions are slower than small and light ions. For example Cl^- ions can theoretically move twice as fast as SO_4^{2-} ions [Ottosen and Hansen, 2016]. A lower conductivity in the electrolyte within the pore structure will result in higher impedance measurements. This difference in impedance value can also be related to the concentration of salt within the stone, as previously shown in this chapter, Figure 6.11.

In real world cases it is also possible to be confronted with a combination of multiple salt ions. How this will impact impedance measurements will depend on the ions present and their individual concentration. As already demonstrated here, more salt will result in a higher impedance value. The magnitude of impact a mixed salt solution will have on impedance will have to be investigated further.

How the environment affects the impedance measurements has not been investigated here, but Lehmann [2018] has done a thorough study on the subject. He states that there are only empirical and semi-empirical formulations that describe impedance dependency on temperature and proceeds to demonstrate that the variation in impedance measurements at room temperature (20± 5°C) is about 15kΩ. Therefore, the impact of temperature is not expected to influence the samples in this study as all experiments have taken place in the lab where the temperature is regulated. Relative Humidity is also investigated, where impedance increases one order of magnitude between 50 to 100% RH. For this study, relative humidity is not expected to influence the measurements, as each experimental system is isolated from its surroundings using cling film. For further studies it is recommended to follow the advice of Lehmann [2018] and always measure temperature and relative humidity when measuring impedance, in order to evaluate if variations are related to these factors.

Based on the results presented in this chapter, it is expected that impedance measurements could be used to monitor a desalination treatment. As salt is removed from the samples, the impedance should increase, nearing values similar to samples saturated with DI water.

7 Monitoring Electro-Desalination using impedance

7.1 Introduction

Based on the research in Section 6, impedance could provide a unique and non-invasive way to monitor salt content and movement within samples. This chapter contains the description and results of an experiment carried out with impedance used to monitor the ED process.

As described in Section 2.2, the ED treatment has previously been monitored through reading from the power supply, where an increase in voltage of the system indicates salt removal. However, as discussed in Section 2.1.4 this method lacks information on what is happening within the rock as the readings concern the full system including poultices. Within this system, salt is moved from one area (the stone) to another (the poultices). Therefore, the measurements are not reflecting salt removal from the samples. Accurate measurements of impedance can be made on the sample only using the setup developed in Section 5.1, eliminating variables not related to desalination of the stone in question.

Chapter 6 concluded that as long as the sample is over 20% saturated with water, and the impedance measurements are under 10kΩ there is likely salt within the sample. In the same chapter, a clear correlation was demonstrated between impedance and salt concentrations, and as such it should be possible to monitor salt migrating out of a sample over time. This chapter contains an experiment that tests the validity of this method for monitoring desalination treatments. Discussion of the results will be presented alongside the results and in an analysis section focused on three themes: comparing impedance to potential difference as a monitoring tool, impedance as an indication of salt content and comparing effects of poulticing to ED treatment. A further discussion of the impact of these results will be presented in Section 8.

7.2 Experimental design

The experiment was designed using the set-up developed in Section 5.1, shown in Figure 7.1.

The ED treatment was applied to the electrodes on the sides of the system through a direct current of 5mA. The resulting voltage from the power supply was noted to calculate the resistance of the system during treatment. After noting the voltage, the system was disconnected from the power supply and weighted to monitor the moisture content. The impedance of the stone sample itself was then measured in the Gamry using an alternating current. The system was then reconnected to the power supply and the ED treatment resumed.

From Section 5.3 it is known that a full desalination of the 5cm core samples of Clashach saturated with $1mNaCl$ takes approximately four days using 5mA. In order to investigate if the impedance values during ED treatment indeed are related to the actual salt content of the sample, several samples were treated with exactly the same ED treatment, with experiments stopped after 24, 48, 72 and 96h. Each sample was then destructively tested using IC and ICP analysis to investigate exact salt content of samples at a given time (Section 3.5.4). Another

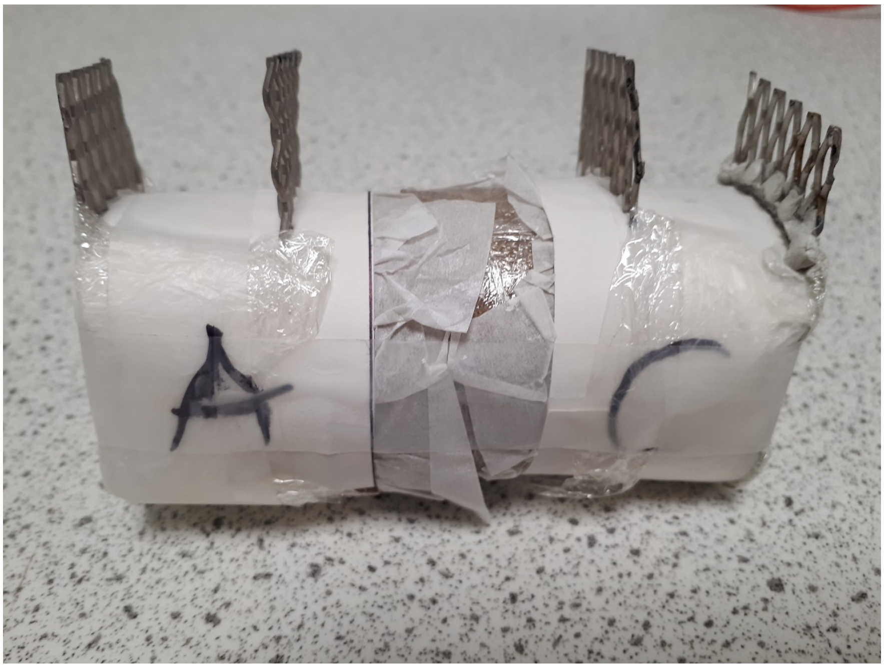


Figure 7.1: *Picture of the experimental system as described in Section 5.1. Electrodes are placed on the outside of the poultice as well as between poultice and stone sample. The entire system is wrapped in cling film to prevent evaporation during treatment.*

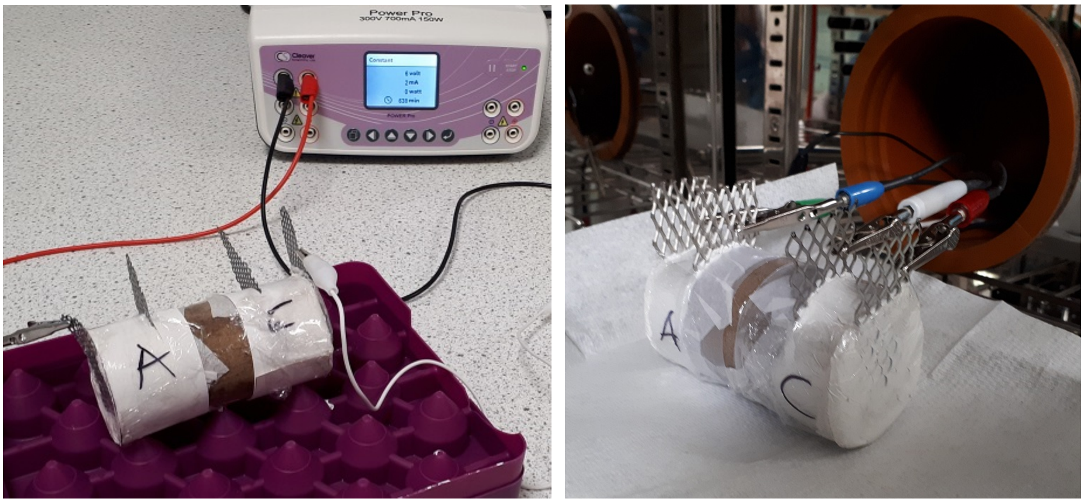
sample treated with poultices only (no electrodesalination) was included to ensure that the effects seen were indeed from ED treatment and not the poultices. A control sample (not desalinated) was also analysed to investigate the starting point of all samples. The treatment protocol for each sample is laid out in Table 7.1.

Table 7.1: *Scheme of treatments for individual samples*

Treatment	Control	24h ED	48h ED	72h ED	96h ED	Poulticing
Sample	C20	C25	C26	C27	C28	C29

Before ED treatment started all samples were tested in the Gamry to measure the initial value of impedance. The control sample that did not undergo treatment of any kind after saturation and impedance measurement, was analysed using IC/ICP to establish the salt content of the samples at the starting point.

In order to ensure stable current to each sample and accurate measurements for the potential difference (voltage), the samples were treated one at a time. All samples were treated with 5mA, during three consecutive weeks to minimise environmental impacts. The clay poultice was not exchanged during the as it affects the water content within the sample (Section 6.3.4). Leaving the clay on for the whole experiment also makes it easier to control the water content of the system. Pictures of a sample undergoing ED treatment are shown in Figure 7.2a and in Figure 7.2b another sample is being measured for impedance.



(a) **(b)**

Figure 7.2: *Sample system during ED treatment (a) and impedance measurements (b). The anode and cathode poultice compartments marked clearly. Electric current is applied to the outer electrodes during ED. For impedance measurements, all electrodes are connected to a sensor. The outer pair is used for applying the electric current and the inner electrodes are used for measuring the impedance of the sample only.*

Every hour during work hours (8am-4pm), three types of data were gathered: (i) the power supply voltage across the outer pair of electrodes was noted; the sample treatment system (Figure 7.1) was then disconnected from the ED treatment and measured for (ii) weight and (iii) impedance across the inner electrodes after placement in the potentiostat. When ED is applied though a constant current (as in this study), voltage is the most commonly used method for monitoring ED treatment (Section 2.2.2). The weight is used to calculate the moisture content of the system as water is evaporated. The impedance is expected to indicate the salt content of the sample. The treatment was executed continuously between work hours without data being gathered.

When the treatment was concluded, the samples were cut using a hammer and chisel into four slices (Figure 7.3a), where Slice 1 is closest to the anode, and Slice 4 is closest to the cathode. Then each stone slice and both poultices (Figure 7.3b) were measured for water content using the weighing method outlined in Section 3.2.4 , to evaluate the validity of the impedance measurements.

After this the samples went through the analysis process described in Section 3.5.4 and their individual salt content was measured using IC/ICP. Conductivity and pH were measured on the leachates (Section 3.5.3) for quality control of IC/ICP measurements and establishing the efficiency of the pH buffering of the poultices.

(a) (b)

Figure 7.3: *Preparation of samples for analysis. (a) Using hammer and chisel to segment samples. (b) Measuring water content on stone slices and poultice.*

7.3 Sample preparation

7.3.1 Initial values for samples

Before the treatment was started, 6 samples (C20, C25-C29) were saturated with $1mNaCl$. Their initial salt content was calculated based on the weight of salt solution absorbed by each sample. The porosity, dry weight before saturation, the weight of saturated samples, the weight of the absorbed salt solution and the calculated salt content are presented in Table 7.2. All samples were saturated with the same salt solution: the variation in amount absorbed is dependent on each sample's porosity.

Table 7.2: *Measured weights for calculating initial salt content of each sample before treatments.*

Sample	Treatment	Porosity [%]	Dry weight before saturation [g]	Weight after salt solution saturation [g]	Weight of absorbed salt solution [g]	Weight of salt [g]
C20	Control	14	209	224	15	0.85
C25	24h ED	12	199	211	13	0.70
C26	48h ED	12	208	221	13	0.72
C27	72h ED	13	206	220	14	0.75
C28	96h ED	12	195	207	12	0.69
C29	Poulticing	12	204	217	13	0.71

7.3.2 Values for control sample (C20)

The control sample was weighed, tested for impedance and then processed (Section 3.5.2). The conductivity, pH and salt content were measured in accordance with the methods described in Section 3.5 and the results are presented in Table 7.3.

Table 7.3: *Measurements for conductivity, pH and salt ion content for the individual slices of the control sample (C20).*

C20		Dry weight [g]	Conduc tivity [μS/cm]	pH [-]	Na^+ content [g]	Cl^- content [g]	Na^+ content [mmol]	Cl^- content [mmol]
Anode	Slice 1	46	2565	8.9	0.066	0.087	2.85	2.46
	Slice 2	58	2644	8.6	0.075	0.110	3.25	3.10
Cathode	Slice 3	42	2682	8.6	0.064	0.086	2.78	2.43
	Slice 4	61	2720	8.1	0.093	0.121	4.04	3.42

The mol concentration should be balanced, as the concentration of sodium and chloride when introduced into the system is 1:1. However, there is constantly less chloride than sodium in these slices. This difference is statistically significant, cannot be explained by the size of samples or by the initial salt concentration measured in a non-salt saturated stone sample. The difference is at maximum 15% of the sodium concentration and is not investigated further.

The total salt concentration measured in the sample ahead of treatment and the average conductivity and pH of the four slices are presented in Table 7.4.

Table 7.4: *Average of measured conductivity and pH of the four slices together with total salt content measured and calculated for the control sample (C20).*

	Average conductivity [$\mu S/cm$]	Average pH [-]	Total calculated salt content [g]	Total measured salt content [g]
C20	2653	8.6	0.845	0.701

The variability between calculated and measured values is discussed further in Section 7.3.3.

7.3.3 The discrepancy between calculated and measured values

The control sample (C20) was tested in the Gamry and then directly processed for analysis. The salt content was then measured using IC/ICP. The calculated salt content was 845mg and the measured salt content was 701mg. This is a decrease in 144mg or 17% from the calculated amount. This difference can be attributed to a few different things; (i) salt could be migrating towards the clay during Gamry measurements based on diffusion, (ii) mass is lost during the cutting process and (iii) the leaching process could not sufficiently leach all salt ions.

Diffusion during Gamry measurments

Diffusion is a slow process and the Gamry measurement only takes a few minutes, so it is unlikely that the main reason behind the discrepancy is this procedure. It could be investigated through analysing the clay used for Gamry measurements, but this has not been done in this study.

Mass lost during cutting process

During the cutting process, 3.7g or 1.65% of the total sample (water, stone, and salt) mass was lost. However, the relative amount of salt, water or stone that has been lost is not known. During the process of cutting the sample there are several processes that might result in loss of overall sample mass. Waste stone dust and chips are produced by the hammer and chisel; water may be evaporating from the sample; salt water may drain from the sample. No water was observed to drain from the sample, and the volume of chips was equivalent to a few sand grains. Evaporation should be relatively minimal at room temperature and relative humidity. The variability of the dry weight of each slice is low, so there is no reason to believe that there are heterogeneities within individual samples large enough to affect the results.

The initial water content of the sample was 14.5g (6mass%), based on the amount of salt solution present. The total amount of water that was evaporated in the oven from the four segmented pieces of the control sample was 13.2g. Therefore, 1.3g, or 9% of the total water content was evaporated during the cutting process.

With 1.3g of the total mass loss of 3.7g being water, 2.4g must be stone and salt. Initially, the ratio of salt to stone is 0.004. As there is no reason to believe this ratio to have changed significantly until this point, the loss of salt resulting from the cutting process should be approximately 10mg of salt. That is less than a tenth of the total discrepancy between calculated and measured salt content.

Leaching

Based on these rationales, the largest change in salt content takes places during leaching, estimated to 134mg, 93% of the total difference of salt content. This could be attributed to some salt not leaching out, or possibly that some salt has precipitated within the sample. Future work could investigate this through SEM or EPMA backscatter, where precipitated salts might be identified. It would also be possible to consider a different approach to the leaching process to ensure complete extraction of salt ions. For the purpose of this study and these results it is only important to mark that a difference in calculated and measured salt content can amount to 17%.

7.4 Results

This section contains data gathered during experiments (Voltage development, Moisture content and Impedance measurements) as well as data resulting from analysis of the processed samples and poultices (Salt content and Conductivity/pH).

7.4.1 Voltage development

Noting the development of the electrical potential difference (voltage) when applying a constant current is the currently accepted method for monitoring the ED treatment. As the salt content of the system decreases, the resistance in the system goes up and the voltage increases. The implications of this were discussed more in depth in Section 2.3. The voltage results for the experiments are presented in Figure 7.4.

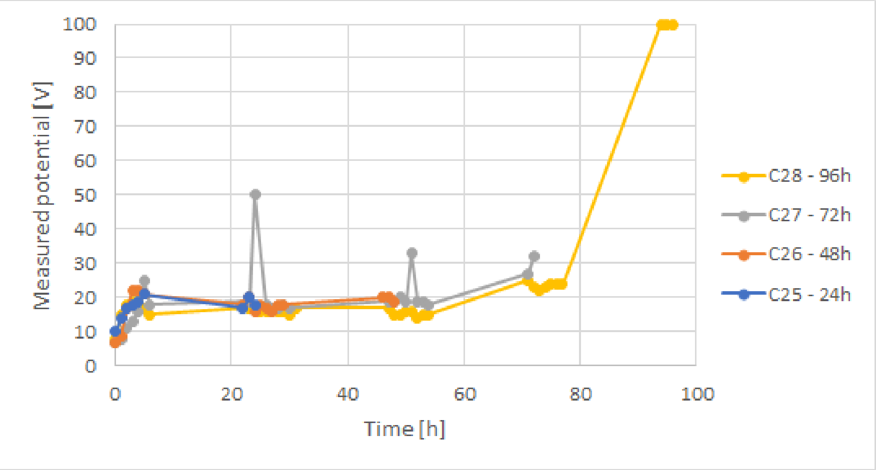


Figure 7.4: *Voltage development of all samples over time during ED treatment*

All samples show a similar increase in voltage over the first couple of hours, and remain at approximately 20V afterwards. Using Ohm's law (Section 2.2.2), this indicates that the system resistance is ca. 4kΩ. Sample C27 has some sporadic peaks before returning to the stable value of 20V. This most likely stems from a bad connection in the electrodes, as was discussed in Section 5.3. This is usually solved through squeezing the electrodes and clay together or taping the electrodes to the clay forms. There is a sharp increase in observed voltage in the last hours of treatment for the 96h sample. The final resistance of the system is calculated to 20kΩ.

7.4.2 Water content development during treatment

When applying ED, water leaves the system in different ways. Initially, water is transported to the cathode due to electroosmosis (Section 2.2). Some of this water leaks out of the poultice compartment during the first couple hours of treatment, which is expected based on previous experiments (Section 5.3). Water molecules are also separated due to electrolysis (Section 2.2). Finally, evaporation also takes place, even though the system is wrapped in cling film in order to slow evaporation down as much as possible. As treatment is administered, the weight of the system was measured before every impedance measurement. The initial weight consists of the fully salt solution saturated samples and the fresh poultices, the poultice compartments and the electrodes as well as the cling film that surrounds it all. If the weight is changed, the only thing that is altered is the water content.

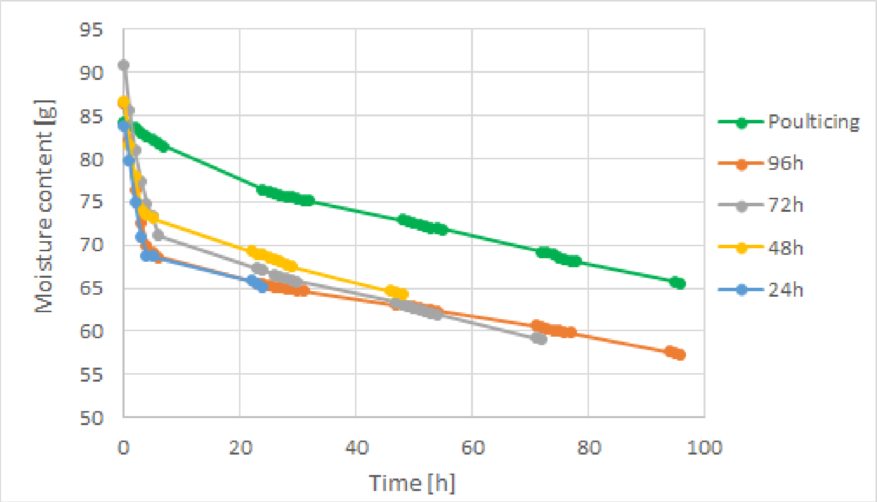


Figure 7.5: *Measured water content of all systems over time during treatment, including poulticing sample.*

The initial water content can be calculated through adding the water content for each poultice and the water content of the absorbed salt solution in the sample. By subtracting the difference in weight of the entire system to the initial water content, the development of water content within the system during treatment can be estimated and is displayed in Figure 7.5. For the first 5 hours of ED treatment 15g of mass is lost. This can be largely attributed to water leaking out of the cathode clay compartment. This is about 20% of the system's total water content, as the system contains about 85g of water at the start of the treatment. This is not the case for the sample treated with poultices only. Instead, this sample follows an approximately constant drying rate throughout the treatment of about 0.2g/h.

After the initial drop in water content for the ED treated samples, they too follow a constant drying rate similar to the rate of the poulticing sample. Here, water is no longer observed to be leaking out in liquid form from the cathode compartment, the loss of water therefore mostly takes place through evaporation and/or water separation within the sample.

Despite wrapping the system in cling film, evaporation can still take place, particularly at the point where the electrodes are inserted into the poultice compartments. This can be conceived by looking at the system shown in Figure 7.1. It is known from Section 2.2 that electrolysis leads to water separating into hydrogen (H^{+}) and hydroxide (OH^{-}). As these ions are charged, they will move within the system towards the electrode of opposite charge. This will result in a pH change where the anode becomes more acidic and the cathode becomes more basic. This can be confirmed by looking at the pH of the system components presented in Section 7.4.5.

The moisture content of the systems does not drop lower than 55g. However this is for the entire system including the poultices, so extra data is needed to ensure that the samples' water content does not drop below the 20% required for the impedance measurements to be reliable (Section 6).

The initial moisture content of the samples is calculated based on the amount of salt solution absorbed by the sample. The final moisture content of each sample is measured at the end of each experiment (Section 3.2.4) and a final moisture saturation can then be calculated (Section 6.2). The results are presented in Table 7.5 showing that none of the samples have a moisture saturation close to 20%.

Table 7.5: *Water content and moisture saturation of samples. The final moisture content of the samples is measured, while the initial water content and final saturation are calculated.*

Sample	Treatment	wc before [g]	wc after [g]	Saturation after [%]
C25	24h ED	12	9	76
C26	48h ED	12	8	68
C27	72h ED	13	6	45
C28	96h ED	12	6	50
C29	Poulticing	12	9	76

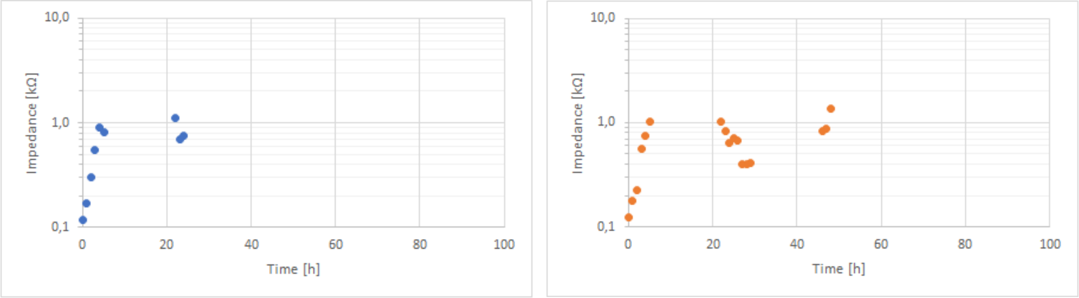
All samples have a reduced moisture content. The poulticing treatment (96h) and 24h ED treatment reduces the water content of the sample to the same degree, and the longer ED is administered, the more water is removed from the sample. However, the moisture saturation limit (20%) required for impedance to reflect salt content only (Section 6.3.3) is not reached for any of the samples, even without adding the 9% of moisture content that is lost during the analysis process (Section 7.3.3).

7.4.3 Impedance development

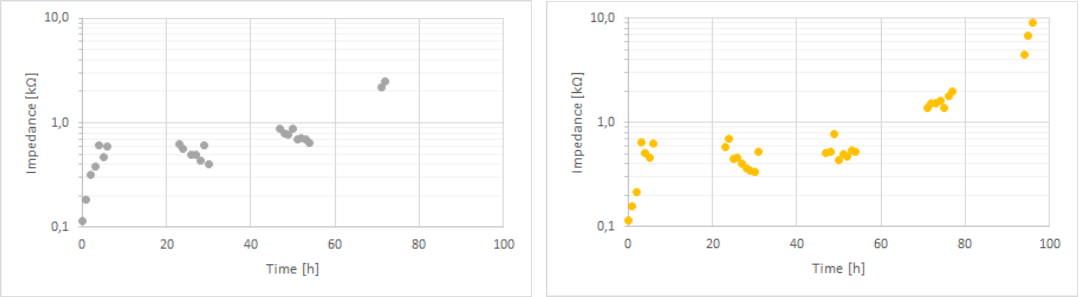
As it has been demonstrated than none of the samples went below 20% moisture saturation, the measured impedance for each sample during ED is presented in Figure 7.6.

All samples show similar behaviour throughout the experiment. In all cases, a steep rise in impedance is seen for the first six to eight hours. Because data were only collected during the lab's working hours, there is gap in data from 8 to 24 hours, so it is not possible to say how the impedance develops during these times. For all samples impedance decreases from 24-32 hours. A slower overall increase in impedance is seen between 32 and 80 hours, with a sharp increase in the final 96 to 104 hours of treatment. In order to illustrate the similarity in this data, Figure 7.7 shows all samples data in the same graph.

From this data it is clear that all samples follow a similar trend. This can be divided into three parts, illustrated by red vertical lines on the graph. The initial phase is the sharp increase in impedance during the first day of treatment. In the second phase during day 2 and 3 of treatment, the impedance is in the range of 500 and 1000Ω. For all samples, a decrease in impedance is seen from morning to afternoon day two. The same tendency is seen for one sample on day three as well. This is not the case for the sample that is treated with poulticing



(a) *24h* **(b)** *48h*



(c) *72h* **(d)** *96h*

Figure 7.6: *Impedance development during the ED treatment for each individual sample*

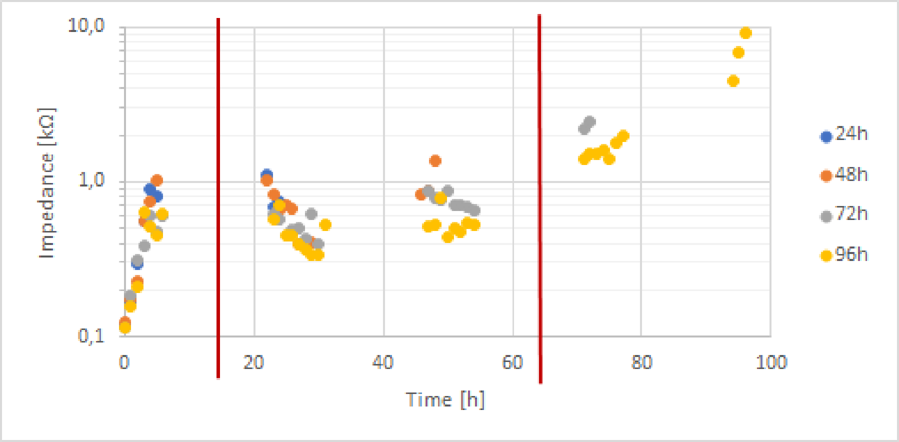


Figure 7.7: *Impedance measurements during ED treatment for all samples.*

only (Figure 7.8) so the results are linked to the ED treatment. It could be the result of back diffusion, but most likely it is the result of handling the sample during the daytime measurements. The poulticing sample is not handled as much as the ED treated samples are. The last phase takes place from somewhere during day 3 of treatment until completion, where a sharper increase in impedance is seen.

Impedance was also measured of a sample that was only treated with poulticing, the results of which are shown in Figure 7.8. In comparison to the ED treated samples, the poulticing results show a slow and steady increase in impedance. After 96h of treatment it reaches a similar level

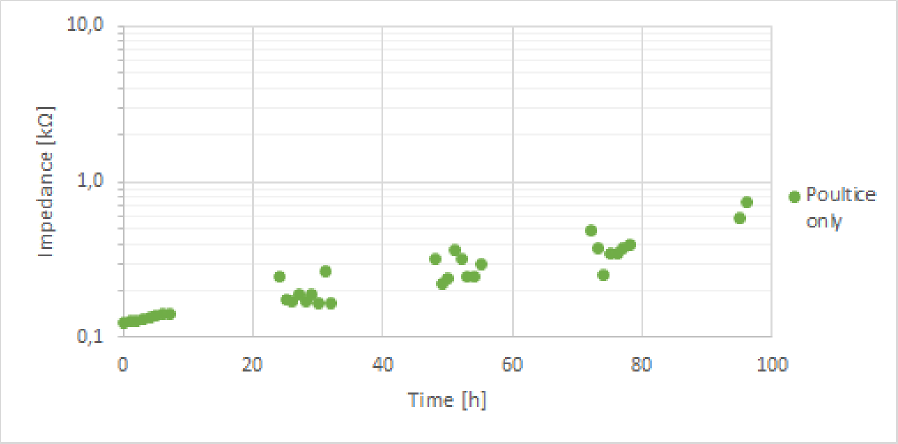


Figure 7.8: *Impedance development for the poulticing only sample.*

of impedance that the ED treated samples do after ca. 4 hours. A deeper analysis of these results will be presented in Section 7.5.

7.4.4 Salt content

The success of the treatments, and the distribution of the ions within the sample is determined by IC and ICP analysis (Section 3.5.4). The salt content of the samples after treatment is presented in Table 7.6, together with the calculated initial salt content and the percentage reduction of salt after treatment for each sample. For all treatments, there is a significant salt reduction over time, illustrated in Figure 7.9.

Table 7.6: *Salt content before and after treatments together with the total salt reduction for all samples.*

Sample	Treatment	NaCl content start [mg]	NaCl content after [mg]	Total salt reduction [%]
C25	24h ED	698	282	60
C26	48h ED	723	213	71
C27	72h ED	749	63	92
C28	96h ED	690	23	97
C29	Poulticing	713	310	57

During the first 24h, salt is removed at 17mg/h. For the following days the salt removal rate is averaged at 3mg/h. The biggest impact of ED treatment is during the first 24h, but in order to reach successful salt removal in accordance with Önorm [1999], the treatment needs to be administered longer. As presented in Section 3.6.2, the ED treatment can be considered a success if the chloride content is reduced to below 0.3mg/g. Any concentration over 1.0mg/g is unacceptable and anything in between would require individual assessments to establish if

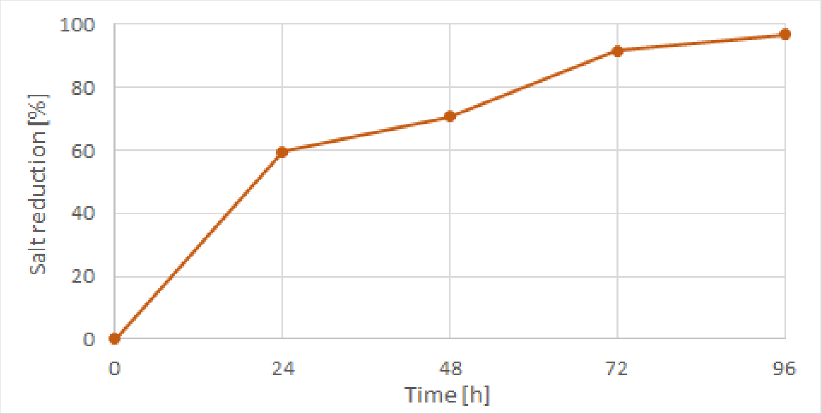


Figure 7.9: *Salt reduction during ED treatment plotted over time where each data point is a different samples final salt content.*

further intervention is needed. The final chloride concentration for all samples is presented in Table 7.7.

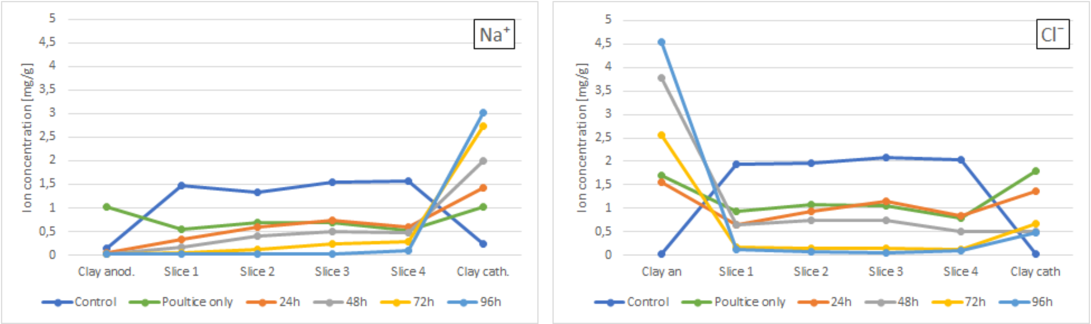
Table 7.7: *Final Chloride concentration for treatments, presented in mg/g, in order to compare to success criteria presented in Section 3.6.2.*

Sample	Treatment	Dry weight of sample [g]	Cl^{-} content after treatment [mg]	Final Cl^{-} concentration [mg/g]
C20	Control	209	578	2.77
C25	24h ED	199	172	0.87
C26	48h ED	208	134	0.65
C27	72h ED	206	28	0.14
C28	96h ED	195	16	0.08
C29	Poulticing	204	190	0.93

The initial chloride concentration is more than 2.5 times higher than the acceptable level of 0.3mg/g. All treatments reduce the chloride concentration below 1.0mg/g and by 72h a of ED treatment the chloride concentration below the acceptable level of 0.3mg/g. This means that for these samples, a salt reduction of 92% is sufficient to reach accepted levels of chloride content. Successful desalination can therefore be considered to have taken place after 72h, but an almost complete reduction in salt was achieved by 96h.

From the data presented here, it is clear that ED is an effective method to remove salt from stone, and that the biggest reduction of salt takes place within the first 24h of treatment. In Section 7.5 the salt content will be further analysed together with impedance measurements.

The distribution of the salt and sodium and chloride ions through the samples measured from the 4 rock slices and the poultices taken after treatment is illustrated in Figure 7.10. The control



(a) *Sodium concentrations* **(b)** *Chloride concentrations*

Figure 7.10: *Ion concentrations measured through IC/ICP in samples before (control) and after treatments.*

sample (C20) and initial clay values represent the values before treatment. The concentrations are presented in mg of ion per g of slice/poultice because samples vary slightly in size.

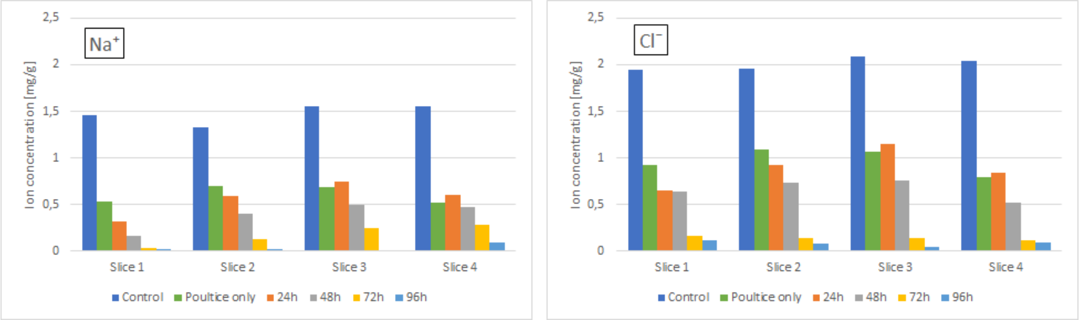
These graphs confirm that any treatment lowers the concentration of salt ions within the stone samples. An increase of positive ions in the cathode clay and negative ions at the anode clay over time is also visible. This shows that the ED treatment has been working as expected.

To investigate the salt distribution within the stone samples, a closer look at the ions contained in the stone slices is presented in Figure 7.11. Apart from sodium and chloride, calcium and sulphate have also been measured, in order to evaluate the probability of new salts precipitating (Section 2.2.4).

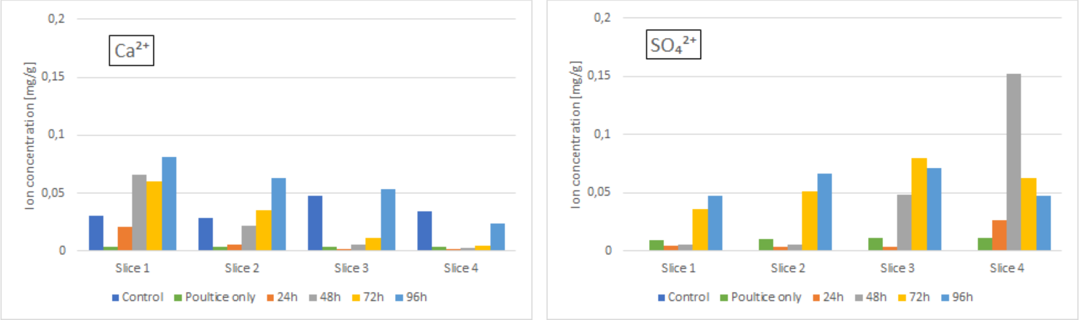
From Figures 7.11a and 7.11b, the decrease in $NaCl$ is clear for all treatments. The discrepancy in sodium and chloride concentration is attributed to the ions' atomic weight. As is clear from these graphs, the ED treatments have successfully reduced the ion content in all slices. The longer a treatment is applied, the lower ion content is measured throughout the samples. However, there is no clear trend that indicates ion separation in a way that can be compared to Figure 8.5. This could be due to the size of the samples. In previous studies [e.g. Andersson, 2017a; Norsk and Andersson, 2016; Skibsted, 2013] larger samples have been used and the data have corresponded to the schematic of the separation of ions.

Figure 7.11c shows calcium present in the stone before treatment. For the poulticing only sample, no calcium is left after the treatment. For the ED treated samples an increase in calcium is seen over time, especially towards the anode. This indicates the release of calcium because the poultice is effectively neutralising the acid created at the anode. This is corroborated by the pH measurements presented in Figure 7.12b.

Sulphate enters the samples from the poultices over time. Figure 7.11d shows this with a tendency toward the cathode side of the sample. This is explained by there being more sulphate in the cathode clay, and as a negatively charged ion, it will migrate towards the anode. Sulphate can become a problem if it bonds with other ions, but the low quantities observed here are not



(a) *Sodium* **(b)** *Chloride*



(c) *Calcium* **(d)** *Sulphate*

Figure 7.11: *Ion concentrations for stone slices of all samples. Slice 1 is closest to the anode, Slice 4 is closest to the cathode.*

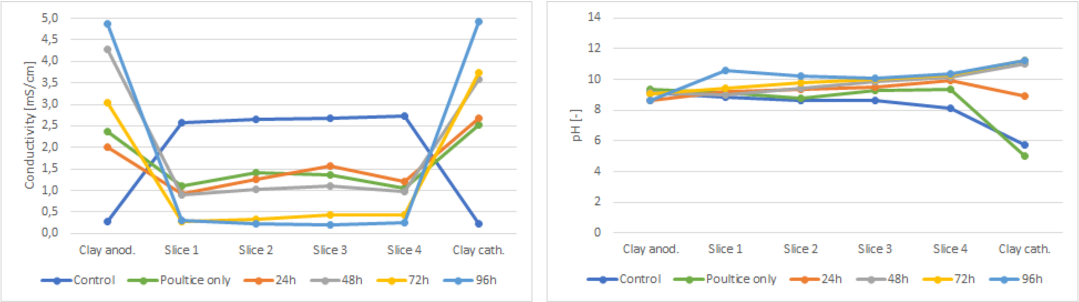
expected to cause further problems [Önorm, 1999]. A high value is seen in Slice 4 for the 48h sample. This can not be explained by measurement errors as two tests are taken for each sample and both were the same. The IC/ICP measurement has also been corroborated by the conductivity measurement. It is more likely that if a handling mistake has been made, it happened before or during the leaching process.

Overall the amount of calcium and sulphate found in these samples is below 0.1 mg/g sample and therefore not likely to be a problem for the treatment. The lowering of both sodium and chloride over time demonstrates the success of the ED treatment.

7.4.5 Conductivity & pH

As well as salt content, conductivity and pH are also measured after completed treatments (Figure 7.12). Conductivity is measured in order to set-up the IC/ICP properly as well as compare any anomalies found in the IC/ICP results. The pH is measured in order to check that no acidification has taken place which damages the stone. The pH also demonstrating the functioning of the electrolysis process.

From these graphs there is a clear decrease in conductivity throughout the stone over time, while there is a steady increase in conductivity in the poultices. This indicates salt being removed



(a) *Conductivity* **(b)** *pH*

Figure 7.12: *Measurements of conductivity and pH for stone slices and poultices after treatment. Slice 1 is closest to the anode and Slice 4 is closest to the cathode.*

from the stone into the poultices, in a agreement with the results in Figure 7.10.

The importance of pH values for ED treatments is that acidic environments can be damaging for natural stone (Section 2.1.2), and the ED treatment alters the pH environment if no actions are taken (Section 2.2). The pH is initially around 8 for the samples and anode poultice, and around 6 for the cathode poultice. For the poulticing only sample pH does not change much. For the samples treated with ED, pH increases over time in the sample to ca. 10 and in the cathode clay to ca. 11. The increase in pH indicates an increased amount of hydroxide (OH^-) ions within the system. This is explained by the separation of water molecules due to electrolysis (Section 2.2). There is no decrease in pH as a result of accumulating hydrogen (H^+) ions. This is because the poultice at the anode contains $CaCO_3$ as a buffer, further explained in Section (2.2.2). The success of the pH buffer can be seen both in the pH measurements, as well as the accumulation of calcium ions in Figure 7.11c. No damage to the stone is expected based on these results.

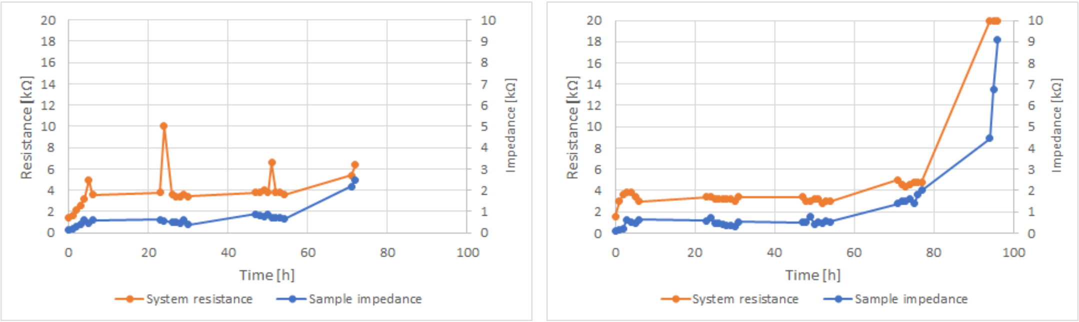
7.5 Analysis

This section addresses the implications of the above presented results, and the possibility of the development of an impedance based monitoring technique for ED and salt detection.

First the monitoring methods of potential difference (voltage) and impedance will be compared. Next, relations between impedance and salt measurements are evaluated. Lastly, the effects of the ED treatment will be compared to the effects of poulticing.

7.5.1 Comparison of potential difference and impedance as monitoring tools

One of the questions posed in this study is whether measuring the impedance of the sample would be a more suitable monitoring tool for ED treatment than the potential difference of the system. The impedance is measured over the stone sample only, and is presented here as the magnitude of the complex impedance. The resistance of the entire system is calculated from the applied electrical current and the potential difference using Ohm's law (Section 2.2.2). The sample's impedance magnitude and the corresponding system's resistance for samples C27 (7h ED treatment) and C28 (96h ED treatment) is presented in Figure 7.13. Although resistance and impedance has the same unit, they are not the same and the impedance data is therefor presented on the right hand axis.



(a) *C27 - 72h* **(b)** *C28 - 96h*

Figure 7.13: *Impedance magnitude for samples C27 and C28 and the calculated resistance of their ED systems based on the logged potential difference during ED treatment.*

Two key differences can be seen from these graphs. First, for sample C27 (Figure 7.13a), peaks can be seen in the system resistance (orange), while no peaks are seen in the sample impedance (blue). This behaviour is common in ED treatments (Section 5.3), and is likely due to a loss in connection between electrodes and clay.

The second point can be seen in the graph for sample C28 (Figure 7.13b). Here, both curves are smooth, following the ideal scenario for both sample and system. The difference between the two techniques can be seen in the last three measurements. While the system resistance (orange) is increased directly from ca. 5kΩ to 20kΩ, the sample impedance (blue) is more slowly increasing, not reaching 10kΩ. Based on the findings in Section 6.3.4, this could indicate that there is still salt left in the system, something that can not be considered based on the system resistance, which is derived from the noted potential difference.

From this it can be concluded that the impedance of the samples are more reliable and more sensitive to the salt movements within the system than the resistance of the entire system.

7.5.2 Impedance as indication of salt removal during ED treatment

It has already been concluded in Section 7.4.2 that the moisture content is high enough within the samples throughout treatment so that the impedance measurements can be relied upon to reflect the salt content only. Figure 7.14 shows the measured salt content of each sample together with their final impedance values.

The data shown in this graph is closely related to the data seen in Figure 6.12, which had the coefficient and exponent of 0.1016 and 0.835 respectively. The variations of these trend lines can

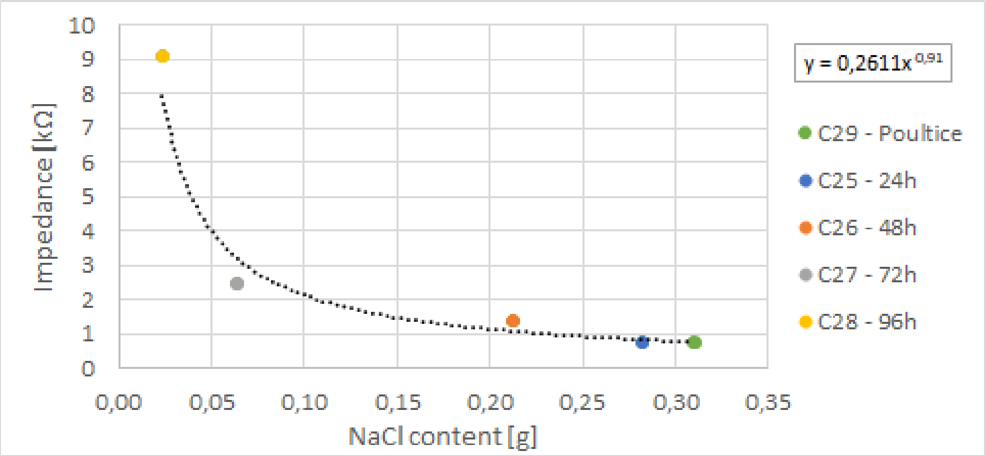


Figure 7.14: *Impedance and salt content of the samples.*

be explained by the discrepancy between calculated and measured salt content, as the analysis process has been proved to loose 17% of the salt content for the control sample (Section 7.3). Nonetheless, it is again clear that a higher impedance indicates a lower salt content.

As was discussed in Section 6.4, complete removal of salt ions from a sample is indicated by impedance values of 10kΩ and above, for these samples. None of the samples in this experiment reach this value, and neither is all of the salt removed. Looking at Figure 7.13, the impedance is increasing steadily and had the treatment continued longer, it is expected that complete salt removal and an impedance of 10kΩ would be reached (Section 5.3). However, the increase in impedance between samples C27 and C28 is threefold, while the salt content is decreased from $0.06g$ to $0.02g$. This relationship between salt content and impedance ensures that for even for small amounts of salt, high values of impedance are not achieved until a certain point. In this study, only when the salt content is below 0.01% of the total mass of the sample, is the measured impedance above 10kΩ (Section 5.3).

The function found for the relationship between salt and impedance in Section 6.3.5 was $y = 0,1016x^{-0,835}$. Using this equation and the impedance values measured for sample C28 that was treated with ED for 96h, the salt content can be estimated for each data point. This is presented in Figure 7.15 together with the measured salt content of each sample in this experiment.

All measured values are close to the estimated values on this graph. However, without data concerning the first hours of treatment it is not possible to say if the relationship between salt content and impedance is a good fit throughout the entirety of the treatment. The difference in estimation and measured values could be explained by the discrepancy between actual and measured salt (Section 7.3), as some salt is lost in the process of cutting and sample preparation before the salt can be measured. For sample C20, 0.14g is lost between the saturation of salt solution and the final IC/ICP measurement. The difference between the measured and estimated salt content is less than this value. Therefore it can be concluded that this estimation

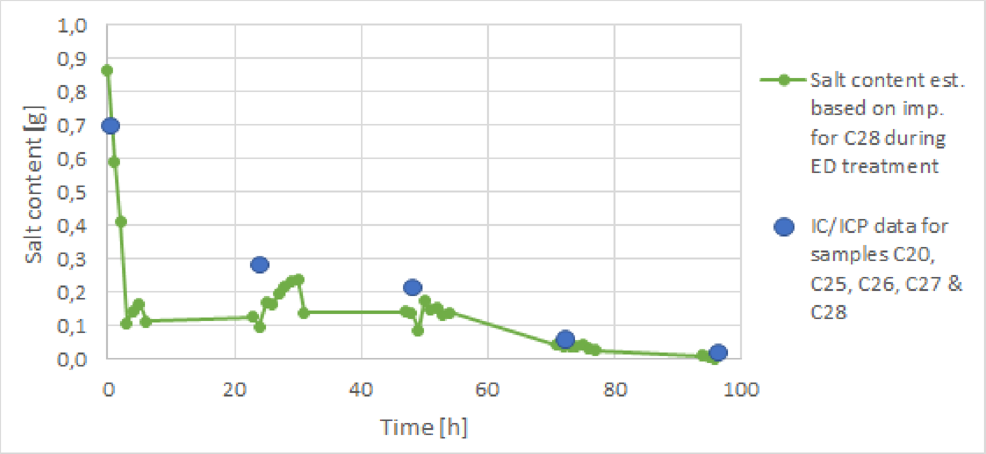


Figure 7.15: *An estimation of salt content based on impedance values measured during the experiment for sample C28, using the function found between salt and impedance in Section 6.3.5,* $y = 0,1016x^{-0,835}$*. The measured salt content using IC/ICP for the individual samples after treatment is presented as well.*

curve for salt content based on impedance is accurate.

7.5.3 Comparing poulticing only to ED treated samples

In order to confirm that the effects seen in the experiments were indeed from the ED treatment and not from the application of poultices, one sample was treated with poultices only for 96h. The impedance measured for this sample is plotted together with the impedance for the 96h ED treated sample in Figure 7.16.

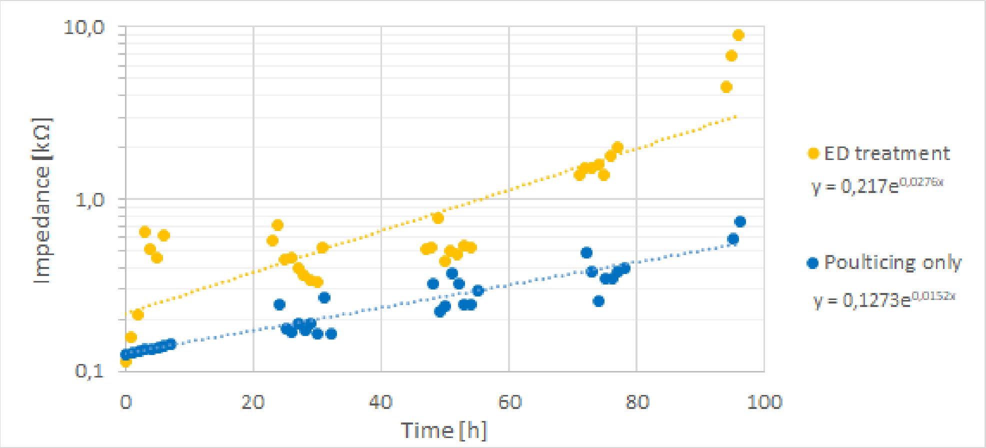


Figure 7.16: *Impedance for samples treated for 96h, one with ED, one with poultices only.*

The impedance development for these two samples are very different. The ED treated sample has a steep increase for the first six hours of treatment, then plateaus, to then increase again by the end of treatment. The poultice-only sample has a steady slow increase in impedance to end on a value similar to the value measured after only 24 hours of ED treatment. This indicates that the behaviour of the salt within the ED treated sample is very different from the poultice only sample. It is clear that the effects seen in the experiments is not a result of applying poultices to the samples, but instead is due to the ED treatment.

The efficiency of the treatments can be further investigated by using the calibration curve found in Section 6.3.5 for estimating salt content of the two samples, presented in Figure 7.17.

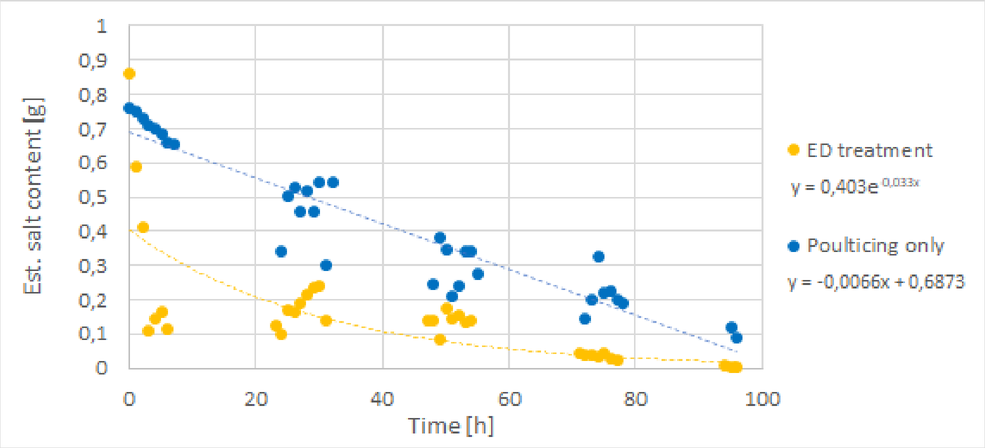
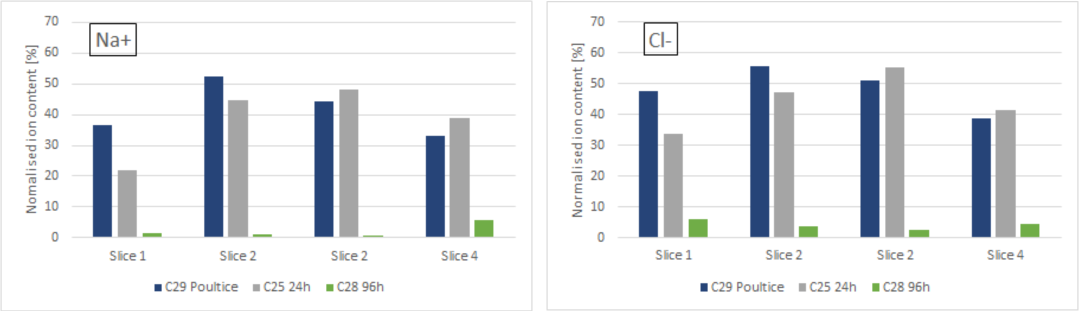


Figure 7.17: *Salt content estimations for an ED treated sample and poulticing only sample, based on the measured impedance and the calibration curve found in Section 6.3.5.*

As is expected, the poulticing treatment seems to be removing salt at a linear rate, while ED has a more exponential reduction in salt content. This graph demonstrates how impedance measurements could be used to estimate salt content on sites outside of the lab where IC/ICP measurements are not available or possible.

The final comparison of the two treatments is the measured salt content at the end of the treatments. Figure 7.18 shows the normalised ion content of the stone slices after treatment for the poultice-only sample (C29) and two ED treated samples, C25 (24h) and C28 (96h).



(a) *Sodium content* **(b)** *Chloride content*

Figure 7.18: *Normalised, final ion content for three samples from the experiment.*

In these graphs, it is quite clear that there is a similarity in salt content for the 24h ED treated sample and the poultice-only sample. This means that treating a sample with poultices for 96h is as effective as applying electricity for 24h. 96h of ED treatment is a significant improvement in salt removal compared to poulticing only.

It is important to state that poulticing is a complex method (Section 2.1.4), which has not been fully researched in this study. Poulticing requires individually specified poultice(s) for each situation and which ED does not. As the purpose of this experiment was only to ensure that results were reflecting the ED treatment and not any poulticing effects, the clay was not optimised for the poulticing method. Any direct comparison between the effectiveness of the two methods can therefore not be made here.

8 Discussion

8.1 Summary

8.1.1 New experimental methods

Dividing samples into 4 for salt movement detection
The samples have been divided into four 1.25cm thick slices to detect the movement of ions within each sample. No variations in sodium and chloride ions were observed between slices (Section 7.4.4). This fine segmenting of small samples has previously been done with successful results [Ottosen, 2016]. However, a lower electrical current was applied (2mA) in Ottosen's experiments. It is likely that the increased current of these experiments acted more quickly to remove the salt ions (Section 5.2), which prevented a gradient in ion concentration from being detected. To investigate ion movement during ED treatment further, the applied electrical current must be considered in relation to the sample size.

Four electrodes instead of two
This study has presented a new electrode set-up for ED treatment, using four electrodes instead of two. This facilitates monitoring of the stone sample only, instead of the entire system (including the poultice). Previous studies have presented an approach to make the treatment more efficient using three or four electrodes [e.g. Feijoo et al., 2018a; Feijoo et al., 2018c], but the use of added electrodes to monitor the treatment has not been tested before. Precise, non-invasive monitoring of ED treatment is a novel application of Electrochemical Impedance Spectroscopy (EIS). The accepted method for investigating the development of the treatment is to measure the voltage (if electrical current is applied, otherwise reversed) across the entire system, including poultices. The EIS measurements are a more precise and reliable measurement of the desalination treatment than voltage as with this set-up it can be measured across the sample only.

Impedance as salt content indicator
A series of experiments have been carried out that defined a relationship between impedance values and salt content, shown originally in Figure 6.12 and repeated here as Figure 8.1. The curve follows a power law function, with increasing impedance for reduced salt content, with a good fit for the data.

The trend-line from Figure 8.1 ($y = 0,1016x^{-0,835}$) was used to estimate the salt content of a sample undergoing ED based on the measured impedance, shown as the green line in Figure 8.2 (Previously presented as Figure 7.15). Similar samples were also treated with ED and every 24 hours one was destructively processed, and the salt content was measured using IC/ICP (blue dots in the same figure).

Firstly, the two datasets (calculated salt content in green and measured salt content in blue) follow a similar curve which indicates that the calculation of salt content is functional. However, there are discrepancies. The first data point is different because the function used to estimate

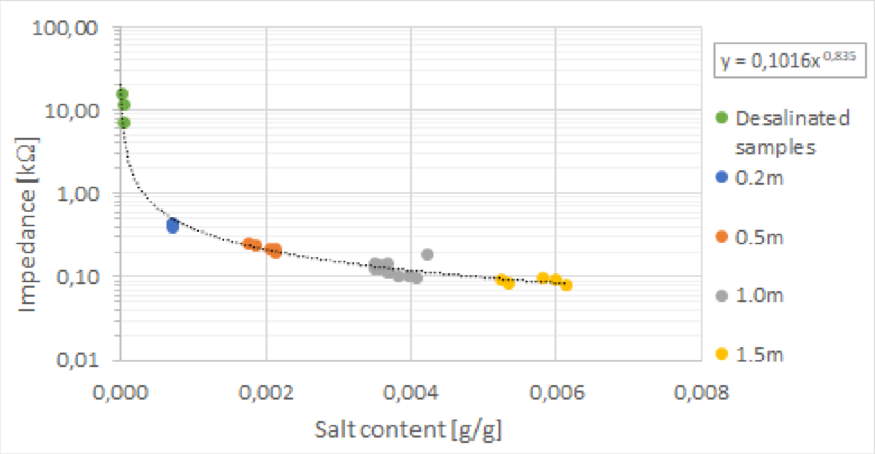


Figure 8.1: *Impedance of samples with varying salt concentrations, including desalinated samples containing <0.01g$NaCl$.*

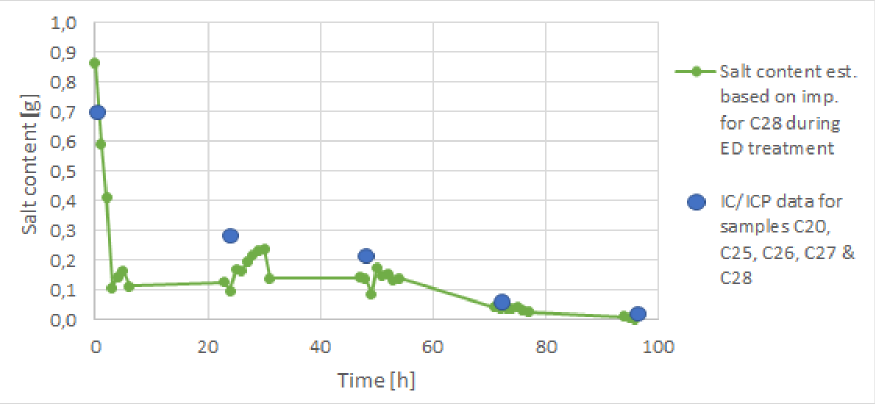


Figure 8.2: *An estimation of salt content based on impedance values measured during ED trial for a sample, using the function found between salt and impedance in Section 6.3.5, $y = 0,1016x^{-0,835}$. The measured salt content using IC/ICP for the individual samples after treatment is presented as well.*

salt content is more accurate for higher salt concentrations than lower. This can be explained by there being more samples of high salt content that provided the base for the trend-line used for estimations. The higher salt concentration measured than calculated for the other data-points has two explanations. A lower concentration of salt has also been measured in the IC/ICP compared to the calculated salt content for samples not undergoing ED treatments (Section 7.3.3), likely due to loss of material during the analysis process. Also, the temperature of the stone treated with ED will increase, resulting in an impedance decrease. This will lead to a lower estimation of salt content than the actual salt content.

To the author's knowledge, using impedance to estimate salt content in building materials has not been done before, but relating impedance to salt concentration of solutions is a well-established method [Lima et al., 2017] and similar curves have been found for $NaCl$ in the past

[Badhe and Helambe, 2013]. Based on the results of this study it is therefore worth pursuing this method further.

At what salt content/impedance is desalination considered completed?

One way of determining complete desalination is to compare the final salt content as a percentage of the original [Ottosen and Hansen, 2016]. It could be argued that this is only an indicator of effectiveness rather than success, as this is entirely dependent on the initial salt content and there could still be damaging levels of salt within the stone. Another way to determine desalination is to compare the final salt content with the salt content limits set-up in a standard such as Önorm [1999] as is done by Ottosen and Rörig-Dalgaard [2009] amongst many others. Here, less than 0.03wt% of chloride ions is accepted, which is equal to ca. 60mg for these samples.

Figure 8.3 (previously Figure 7.14) shows the impedance and $NaCl$ content measured during the trial experiment. Both sample C27 and sample C28 contain less than 60mg chloride (28 and 16, respectively) and could therefore be considered successfully desalinated according to the Önorm [1999] standard.

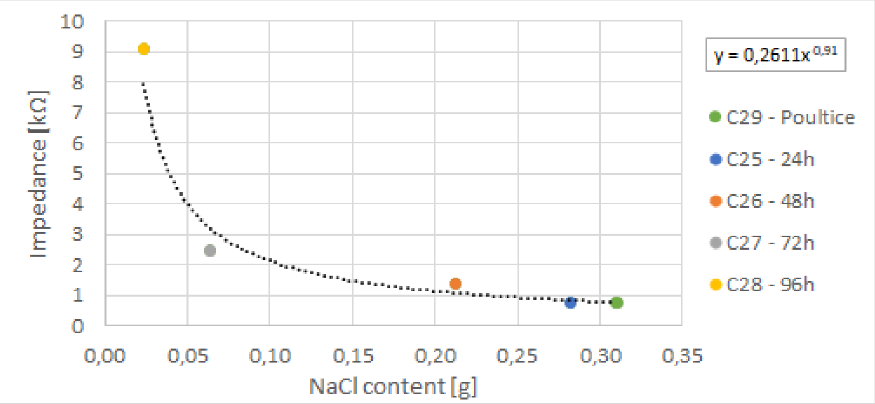


Figure 8.3: *Impedance and salt content of the trial samples*

The dramatic increase in impedance towards 10kΩ for C28 is a very clear indication of a more complete treatment by comparison to the 2.5kΩ seen for C27. Using at least 10kΩ as the indication of a completed ED treatment would help ensure that the treatment is complete. The reduction in salt was 92% for C27 and 97% for C28. Had the treatment continued it is likely that 99% of salt would have been removed as was the case in Section 5.2.2.

Poulticing vs ED

Poulticing is a complex method in which poultice(s) need to be individually assessed and applied for each treatment [Pel, Sawdy and Voronina, 2010]. This is not the case for ED, which makes it a more generally applicable method that requires less expert knowledge to apply.

To rule out the effects of poulticing during experiments in this study, a comparison of salt removal by poulticing to ED has been carried out. This is not a comparison of efficiency between the two methods of poulticing and ED, because for poulticing to function optimally the poultices must be optimised for the object being treated. Rather, this is a control to make sure that the salt removal measured is a result from the ED treatment rather than the application of poultices.

The salt removal for the poulticing treatment follows the expected rate that can be related to reduction through diffusion. The change in rate of removal of salt during ED treatment has not been investigated at this detailed level before, but the total treatment time is in line with several other studies [e.g. De Clercq, Vanhellemont and De Swaef, 2014; Herinckx et al., 2011; Ottosen, 2016]. The results show that poulticing removes the same amount of salt in 96h as ED does in 24h. The accelerated removal of salt in ED compared to poultices has only previously been seen in Skibsted [2013].

Based on these results it was concluded that the effects seen in the ED treated samples were not from the poultices alone, and that the ED treatment is more effective in removing salt from stone.

8.1.2 Impedance dependence on various variables

Porosity
In this study no correlation was observed between impedance and porosity (Section 6.3.2). This is the case for samples of the same sandstone, as well as between the two different types of sandstone. As impedance in porous media is dependent on the connection of the pore network throughout the sample (Section 6.3.2) it is reasonable that porosity is not a factor for impedance as it does not consider the pores' connectivity. Lehmann [2018] found that the pore size distribution was a more likely determining factor for the impedance measurements. Pore size distribution was not measured in this study.

Water saturation
Apart from the dependence on pore connectivity, impedance is also dependent on water content [Lehmann, 2018]. Based on the results in this study, the water saturation of the samples does not affect the impedance measurements as long as saturation is over 20% (Section 6.3.3). As porous materials dry out, there is a connection between the drying surface and the inner pore system through a film layer of moisture (Section 2.1.1). The increase in impedance at 20% moisture content is likely due to the moisture film breaking apart, severing the electrical connection between the electrodes.

Salt content
Several salt concentrations were tested with a clear difference in impedance measured between concentrations (Figure 8.1). The biggest difference however was seen between 0.03wt% of salt (the lowest tested concentration) and DI water, with an increase of impedance values by 10000 compared to a sample containing salt. Similar tendencies were seen in Lehmann [2018], though the salt dependency of impedance was not investigated in any depth.

8.1.3 Desalination phases

The three phases

During the experiments, three desalination phases were observed (Figure 7.7, repeated here as Figure 8.4). The first takes places during the first 8 hours of treatment, where impedance increases quickly from ca. $0.1k\Omega$ to $1.0k\Omega$. The second phase continues with impedance of just under $1.0k\Omega$ for day 2 and 3, with a very slow increase in impedance over time. The third phase shows a steeper increase in impedance after 60h or so of treatment. The final impedance value measured in the trial was $9k\Omega$.

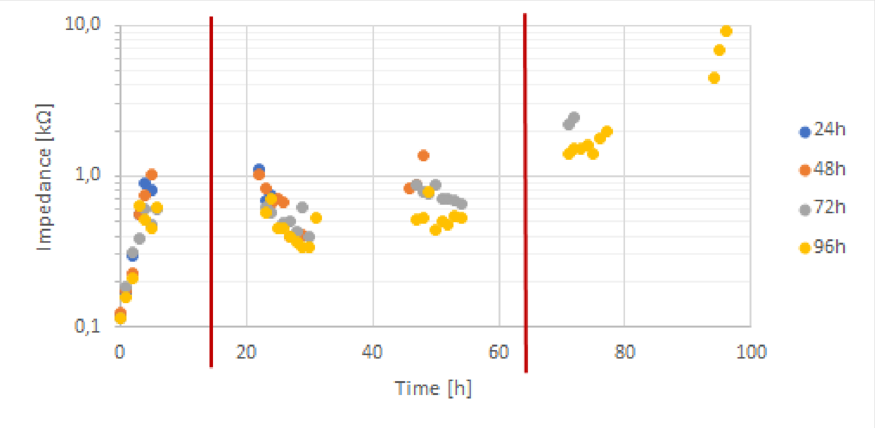


Figure 8.4: *Impedance measurements during ED treatment for all samples.*

A possible explanation for these phases is illustrated in Figure 8.5. At the start of ED, impedance will be low as the salt ions within the sample are mixed throughout, creating an even connection (Figure 8.5a). As the treatment starts, the salt ions close to the surface and their opposite charged electrode will move out of the sample quickly, increasing the impedance. The rest of the two populations of positively and negatively charged ions move in opposite directions through the sample (Figure 8.5b). This creates a continuing connection of ions throughout the sample, keeping the impedance stable. At some point however, there might effectively be a 'gap' between the two populations, when the two populations have passed each other (Figure 8.5c). After this point, impedance will increase because pore spaces towards the centre of the samples contain less ions, i.e. fresh water resulting in an accelerating, third phase. Figure 8.5d shows the end result of the desalination treatment in an ideal situation, which should result in a distinctly higher impedance than if there is any salt present at any place within the sample.

This pattern of salt distribution during treatment has not been confirmed in this study, due to the relatively small sample size of the samples combined with the choice of experimental timing. However, previous studies [e.g. Andersson, 2017a; Norsk and Andersson, 2016; Skibsted, 2013] have observed this pattern for larger samples. More studies are required, with larger samples and a greater number of samples run to more closely spaced timings to investigate this theory further.

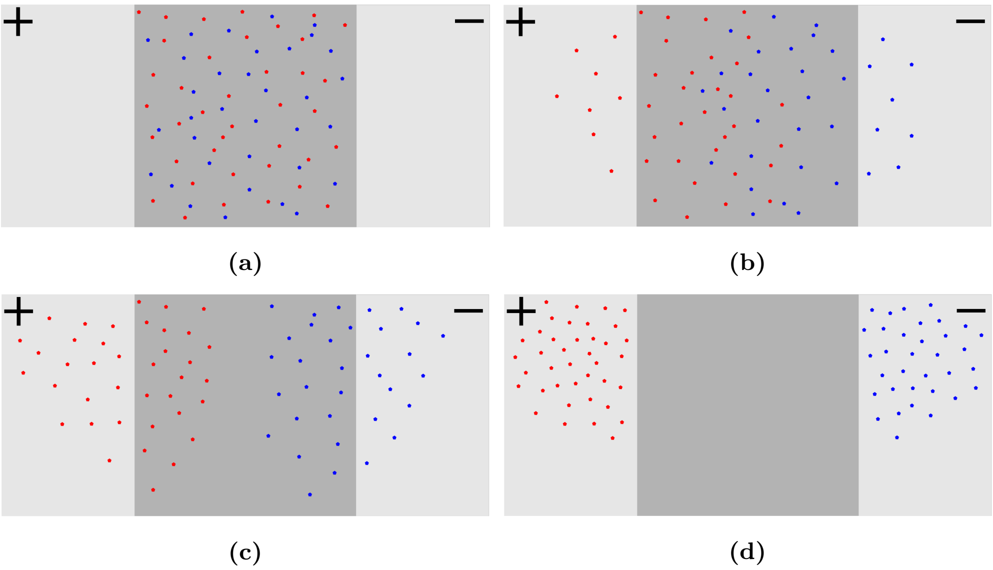


Figure 8.5: *Movement of ions within treatment system where the dark grey is the stone sample and the light grey is the poultices. Red ions are negatively charged (i.e. Cl^-) and blue ions are positively charged (i.e. Na^+). (a) Beginning of treatment, ions evenly distributed in the sample. (b) During first and second phase of treatment, ions separate, moving towards opposite charged electrode. (c) During third phase of treatment, the ion populations have separated from each other, leaving pore space with water only in the middle. (d) Completed desalination, all salt ions are in the poultices, (almost) no salt ions are left within the stone.*

The detailed analysis during ED treatment performed here has not been possible before because the previous monitoring method of reading voltage (if electrical current is applied), encompasses the entire system rather than the sample only. The mechanisms behind the ion migration have however been considered in Ottosen, Dias-Ferreira and Riberio [2015] with emphasis on the importance of both electromigration and diffusion to achieve desalination. The importance of diffusion is reduced as the applied electrical current is decreased and is also dependent on the placement of electrodes on the samples. For an opposite placement, like in this study, the effects of diffusion are deemed negligible.

8.2 Experiments

8.2.1 Variability between measurements

The range of impedance measurements

Based on the data presented in Figure 6.7, the median variation in impedance for individual samples from the mean impedance for all samples while dry was 34%, while it was 32% for wet samples. For samples saturated with salt, the same metric was 10%. This increase in variability could be due to the increased resistance within the samples (Section 2.3.3), variations in temperature within the lab, but it could also be to increased knowledge and ability from the user, as the impedance measurements for salt saturated samples were done much later in the project compared to the dry and wet samples.

Possible errors

There are many variables to consider for impedance measurements that could lead to errors. The connection between electrodes can be disrupted by the poultices detaching from the stone sample or the metal electrodes detaching from the poultices as a result of changes to the poultice as water is either absorbed or evaporated. The packing of the clay needs to be thorough to avoid air bubbles. The ED treatment can result in an increase in temperature within the stone samples which affects the impedance measurement as well. Ensuring that the same procedure is followed for every measurements limits any variations, and meticulous preparation together with continuous control of the set-up minimises any errors.

8.2.2 Further data that could be collected

Data on temperature and RH

For sandstone, the conductivity increases with temperature, so any variations in temperature will affect the impedance. Lehmann [2018] found empirically that the impedance of sandstones can decrease by over 40% for 60°C compared to 20°C, all other variables constant. This variation was largest for wetter samples than dryer (6% compared to 1%). The variation was equally large in the other direction for lower temperatures (0°C). For room temperatures of ca. 20°C, no discernible difference is expected based on temperature differences.

Through this study, neither temperature nor relative humidity were recorded. As the sample systems were wrapped in clingfilm to prevent evaporation, it is highly unlikely that RH affected impedance measurements. While the labs were not temperature controlled, they are kept at a comfortable working temperature year-round so are not likely to vary by more than a few degrees. It is recommended that further studies log temperature and RH to confirm that these variables have not affected the data.

Information on pore-structure

Lehmann [2018] also presented the dependency of impedance on specific surface area, which is relating to the inside of the pore structure. A smaller surface area results in a higher impedance. This is because of the amount of electrolyte that is connecting the electrodes. The pore structure has not been investigated in this study, which could have correlated Lehmann's findings concerning impedance dependence on this variable.

8.2.3 Loss of data

From analysis process (sample mass, water and salt)

During the analysis process, sample mass is lost (Section 7.3.3). From the initial salt content calculations and the measurements of the sample C20 (Section 7) a total of $3.7g$ or 1.65% of mass was lost. It is not clear how much of this loss is sample mass, water or salt and therefore how much it impacts the data.

The material loss was kept at a minimal level using handheld tools, which is slower than power tools but enables more control over sample breakdown. While using a saw or similar, broken off pieces can be sent flying so that they might not get caught and collected.

8.3 Application

8.3.1 Methods

How to use impedance (relative change rather than absolute values)
In this study, most of the measurements of impedance have been done on Clashach sandstone. The impedance measurements on Stanton Moor sandstone samples in Section 6.3.2 showed that the impedance of samples will vary with the type of stone being measured. Therefore, the absolute impedance suggested for determining desalination here, are not directly applicable to other stones. Instead, it would be more meaningful to compare the relative change in impedance. This might be 100 times increase from the original value to desalination as was found in this study, but more data is required to establish a more robust cut-off value.

How to attach clay and electrodes
Depending on the object's geometry, placement of clay and electrodes on heritage objects can be a challenge. Ideally, the electrodes are placed opposite each other to provide an optimal electric field. However, there have been studies showing successful desalination using a parallel setup [Norsk and Andersson, 2016; Ottosen, Skibsted and Præstholm, 2014], as well as desalinating protruding objects not in direct contact with electrodes [Andersson, 2017a; Feijoo et al., 2017]. This is of particular interest when dealing with a sensitive cultural object that cannot be touched due to damage or value.

Another issue of application is placement of poultices on vertical surfaces. To counteract gravity, a clay compartment that is attached with minimal invasive methods has been developed by Ottosen, Rörig-Dalgaard and Villumsen [2008] and Ottosen, Christensen and Rörig-Dalgaard [2012]. By keeping in mind the success of removing salt from protruding object, it should also be possible to extract salt from vertical objects by applying the treatment at its base or a horizontal part of it. This will have to be determined for each individual project, and further studies could investigate the treatable size and effect of electric field that is compatible with a safe and successful treatment.

8.3.2 Materials

Clay recipes
The effect of the treatment is not dependent on the clay recipes, however, eventual side effects like pH changes or added salt ions can be an issue and needs to be addressed before application. Rörig-Dalgaard [2013] has delved into different types of clay recipes for the anode and cathode,

something that was utilised in this study as well. In order to keep the system as simple as possible, without adding undesirable salt ions, no additions to the cathode side clay were made while $CaCO_3$ was added at the anode side. When used for ED treatment, the consistency of these poultices ended up very different, despite having the same initial water content. This is partially because of water moving towards the cathode as a result of electro-osmosis (Section 2.2.1), but also because of the chemical differences of the two poultices. The difference in consistency did not become a major issue in this study, but is worth considering when applying this method further, as it could affect the connection of electrodes to the poultice, and the poultice to the stone.

8.3.3 Location dependability

If in lab

Application of ED and impedance monitoring in a lab is straightforward. For improved control of RH and temperature, which both have an effect on impedance [Lehmann, 2018], samples can easily be placed in an environmental chamber. By controlling these factors, the variations in impedance measurements should be reduced.

If in museum

Inside application is similar to lab setting, with a few key differences. For impedance to be precise, the measurements need to take place without interference of surrounding electrical radiation. In a lab this is done by placing the sample system in a Faraday cage. Even though the object of interest might be inside, it might not fit into a Faraday cage or even be movable. Therefore, impedance measurements in the field could show larger variations than in the lab but might still suffice if enough variables such as ambient temperature and RH were being monitored. It is also conceivable that the same electrode set-up (4 electrode system) could be used to measure the resistance using an Ohmmeter or similar device. This would be less precise, but the difference in magnitude (2 times) between salty and non-salty samples, might be sufficient to monitor the ED process. This would ease the deployment of this method in the field as well as make it more economic, as it would provide the information desired, without using expensive lab equipment.

If outside

Outside provides challenges in the form of weather, with drying and wetting periods and temperature changes which can affect both treatments and measurements. The main concerns for ED treatments are the attachment of the poultice clay as well as salt crystallisation.

If the clay is simply placed on the object of interest without a mechanical fixture as in Ottosen, Christensen and Rörig-Dalgaard [2012], the poultice could simply be washed off by rain, or dried up and fall off from lack of adhesion. This could be addressed using various protection, such as wrapping the poultices up in plastic to prevent it from absorbing or dispelling water. This is however only a delay tactic, as the poultice is connected to the object in question, which will be affected by the weather, which in turn will affect the poultice being administered.

Potentially, this could be addressed by covering part or all the object with plastic as well. This is however not feasible for larger objects such as a building, but perhaps possible if the concern is a particular part of a wall or a statue.

Wetting, drying and temperature also affects salt crystallisation within the pore structure of the stone. This happens independently of any ED treatment but is something to keep in mind as ED also dries out the stone as it is administered. It is possible that water must be added to the stone to keep the desalination process effective or even active.

Finally, there might be an issue for impedance measurements outside as there is possibility for larger temperature and RH changes. Lehmann [2018] did however produce a normalising method to be able to compare impedance data at different temperature and RH.

8.4 Future studies

8.4.1 Other salts and stones

All impedance values measured here are only applicable to Clashach samples of this particular size, as impedance varies with the pore connectivity, with inner surface area of the pore system, as well as the length between electrodes [Lehmann, 2018]. The salt concentration estimations will only be applicable to sodium chloride, as the conductivity of salt solutions vary with type of ions.

In this study, Stanton Moor sandstone was also tested for impedance in order to compare it with the Clashach values. The samples had the same size, and similar porosity, but significantly different impedance values at 100% saturation with DI water. The lower impedance of Stanton Moor than Clashach samples could be explained by the former having a better pore connectivity of its pores or a larger surface area (i.e. having a larger amount of smaller diameter pores [Graham, 2016]). For stones with less connectivity and less surface area than Clashach (such as granite or slates), impedance should be higher. For more porous sandstones and limestones, the impedance should be lower.

The size of an object affects its electrical impedance. The longer path the electrical current has to travel between electrodes results in a larger impedance. By increasing the size of the cross-sectional area that the current is applied to, the impedance decreases [Lehmann, 2018].

The conductivity of salt solutions is dependent on the concentration and type of ions, and the temperature. As the electrical current moves through the solution, available charged ions can help boost the movement. The conductivity of 1mass% $NaCl$ at 20°C is 16.0mS/cm, compared to solutions of the same concentration and temperature such as $MgSO_4$ (7.6mS/cm) and HNO_3 (56.1) [Weast and Lide, 1989]. With a high conductivity, impedance will be low.

A database containing a large number of materials and salts would make impedance more practical as a monitoring method of ED treatments, and possibly help to encourage the use of impedance as a salt concentration measurement tool.

8.4.2 Removal rates

Considering Figure 8.4, the impedance is increased quickly for all samples during the first 8h of treatment. When applying this data to the salt content estimation in Figure 8.2, this indicates that there is a large reduction of salt within the first 8h of treatment. As is known from Section 7.4.4, 60% of the introduced salt has been removed by 24h of treatment, but there is a lack of data to confirm if this reduction takes place at a steady rate over 24h, or is the result of 8h intense removal followed by a slower removal rate.

Investigations of the salt movements in the first 8h of ED treatment would be most useful to understand the desalination process further. This could be done by administering ED to similar samples as the ones in this study, and every hour processing a sample destructively to determine the salt content. The implications of the majority of salt being removed in the first 8h of treatment, if that is the case, would be that ED could be administered for a much shorter time than previously thought in order to be effective. However, it will be important to investigate *why* the largest removal is happening in the beginning, and why the removal rate flattens out over time. This could possibly be due to the three phases of desalination described earlier in this chapter. Identifying the point at which phase 1 transitions to phase 2 would certainly help to characterise the mechanisms behind the phases.

Another line of research would be to treat larger samples and try and identify the salt movement through different areas of the sample over time. This has been done before on larger samples [e.g. Andersson, 2017a; Norsk and Andersson, 2016]. How size affects the treatment time is an area of research that is still unexplored. The key to illuminating this is the applied electrical current, as amperes contains a time component ($A = C/s$).

Electrical current divided by the cross-sectional area of the electrical field is defined as current density (A/m^2). If the electrodes are placed in an opposing set-up, this area is the object that is treated's cross-sectional area. For other electrode set-ups, this requires individual calculations depending on sample geometry. Previous studies have mentioned a maximum current density of 5A/m^2 [Liu and Shi, 2012]. This study has concluded that although it seems possible to treat samples at this level, it is safer for the user to apply 2.5A/m^2, to avoid potential release of chloride gas, as well as possible damage to electrodes which could lead to unwanted effects for the stone. Applying 2.5A/m^2 should be possible for scaling up treatments in the future.

8.4.3 From lab to in-situ

As was discussed in Section 8.3.3, application in the field is different than in a lab. The main issues are in reference to:

- Moisture content
- Temperature and RH
- Poultice application

ED is an effective treatment even with low water content in the stone [e.g. Ottosen and Christensen, 2012; Matyščák, Ottosen and Rörig-Dalgaard, 2014], due to the presence of a connected water film through the pore structure (Section 2.1.1). This was further considered as an explanation for impedance measurements being stable for moisture saturation's over 20% (Section 6.3.3). As Scotland is a wet country, water should not have to be added in order to apply the treatment. However, if impedance all of a sudden shoots up above the expected range based on the database (Section 8.4.1), it would be prudent to check the moisture content, and potentially wet the object or pause treatment. Preventing evaporation would be beneficial to ensure moisture content, either locally to the area being treated, or the whole structure if possible.

In the lab, temperature and RH can be controlled, in-situ, this is not the case. Instead, ambient temperature and RH could be monitored during the treatment. If necessary, the impedance measurements can then be calibrated in accordance with Lehmann [2018] to conceive more precise measurements. However, for monitoring of ED treatments, the variations from temperature and RH are not expected to be so large that if affects the monitoring.

As described in Section 8.3.3 poultice application will be an issue outside as poultices could wash away or dry up and fall off. This could be preempted by using the clay compartments as in Ottosen, Christensen and Rörig-Dalgaard [2012] but they have to be drilled into the surface. Drilling to attach the compartments is currently being done in the grout or mortar around sensitive stone that is something that is already being done today. Either way, each individual object will have to be considered and the optimal way of applying poultices in each specific case will have to be identified.

Apart from these challenges, there will also be variations in impedance outside compared to the lab because of electrical interference. This can be minimised by shutting off any unnecessary electrical equipment during measurements.

Once these challenges are met, a treatment could begin. First, identify the area that is to be treated and decide on the most suitable placement of electrodes. Calculate the size of the area to establish the appropriate current to apply to achieve a current density of 2.5A/m2. Set up poultices, electrodes, power supply, ambient monitoring tools and potentiostat. Measure the initial impedance and estimate the salt content based on the database with a cross-reference of stone and salt type (preferably evaluated from efflorescence to avoid invasive sampling). Begin ED treatment and use the inner electrodes to monitor the effects on the object. When a sufficient increase in impedance have been noticed, remove treatment. This procedure might change after studies into removal rates, or if an automatic monitoring treatment is developed.

8.4.4 Automatic treatment system

The next logical step for developing this monitoring method is to set up an automatic treatment system. This could be done though a set-up shown in Figure 8.6.

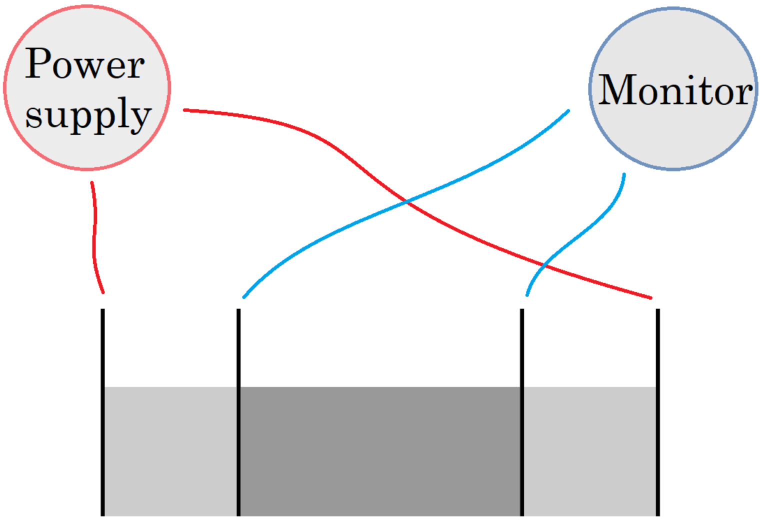


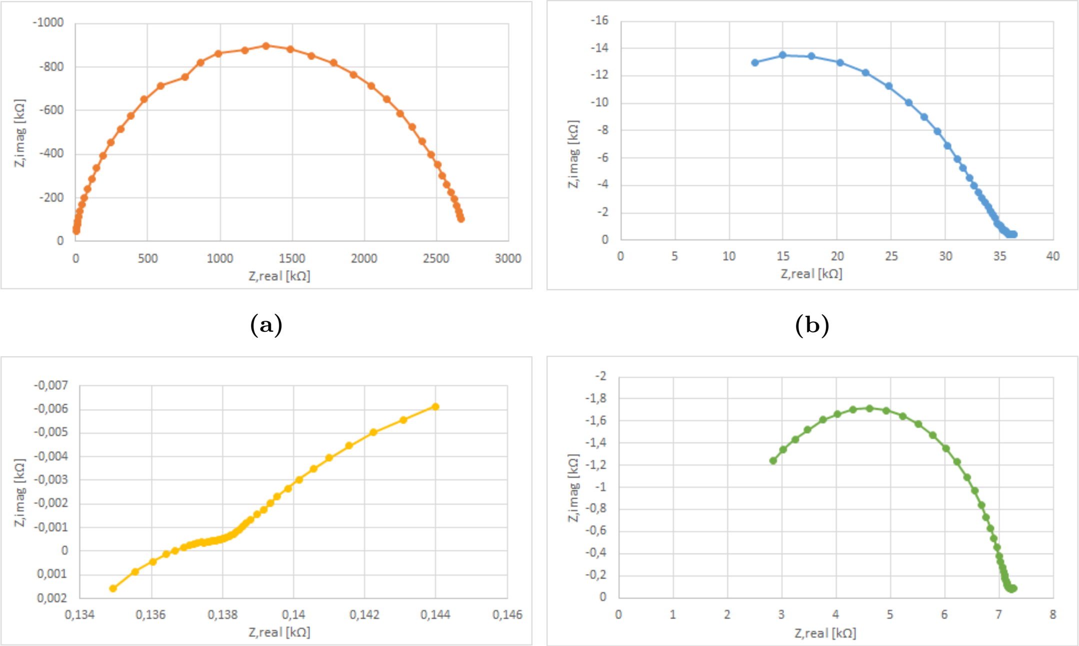
Figure 8.6: *Automatic treatment system set-up. The outer electrodes are connected to a power supply, the inner electrodes are connected to a monitoring system. The monitoring system and power supply can in turn be connected to one another.*

The power supply is connected to the outer electrodes, applying a direct current through the treatment system (poultices and stone). A measurement device (potentiostat, or potentially an ohmmeter) is connected to the inner electrodes to monitor the stone sample only. It would also possible to wire the monitoring device to halt the application of electrical current from the power supply once a certain impedance value was reached. This could prevent the ED treatment from being prolonged when not necessary.

If it was also possible to connect this system to the internet, instant readings could be sent to another location, providing the possibility of a user not having to be present at the site to monitor the treatment. This could ease treatments if many sites are to be treated at once but there are not enough knowledgeable users available for visiting each site simultaneously.

8.4.5 Additional data gathered from impedance measurements

An advantage to using impedance for monitoring compared to resistance is the possibility for obtaining more information using impedance. As was presented in Chapter 2.3.3, impedance is presented with an imaginary and a real part. When doing potentiostatic measurements, as in measuring at a range of frequencies, the data can be presented in a Nyquist plot, with the imaginary part on the y-axis and the real part on the x-axis. the curve of the plot can then be used to determine the electrical components of the system [gamry.com, a]. Examples of Nyquist plots are shown in Figure 8.7. Here, the sample C7 have been measured when it is (a) dry, (b) 100% saturated with DI water, (c) saturated with $1mNaCl$ and (d) having been treated with ED.



(a) **(b)**

(c) **(d)**

Figure 8.7: *Potentiostatic impedance measurements presented in Nyquist plots of sample C7 while (a) dry, (b) 100% saturated with DI water, (c) saturated with 1mNaCl and (d) after ED treatment.*

The frequencies can not be identified on this graph, but from the data it is known that the highest frequencies, starting at 1MHz are on the left hand side on the graph, moving toward the right as the frequencies become lower, ending at 100Hz.

The semicircle shape in Figure 8.7a is common in these analysis, indicating a quite simple electrical system [gamry.com, a]. The curves of the sample when 100% DI water saturated (b) and after ED treatment (d) is very similar, indicating the same electrical component being present. There is a clear difference in the shape of the curve for Figure 8.7c compared to the others. This is because another electrical component have been added to the systems: salt. The curves of the sample when 100% DI water saturated (b) and after ED treatment (d) is very similar, indicating the same electrical component being present.

This data was not further analysed in this study, but is shown here to illustrate the possibilities of expanding impedance measurements to determine the presence of salts in a porous material. There are also other analysis techniques of impedance measurements [gamry.com, a].

9 Conclusions

A new four-point electrode setup has been used for ED treatment, which has enabled measurements of the electrical properties of the stone sample only (rather than the entire assembly including the poultice). The impedance of the sample has a a clear positive correlation as salt is removed. Previously the resistance of the entire system including poultices has been the monitoring method of choice, and in this combined set-up the total amount of salt is fixed. An increase in overall system resistance could be due to the separation of the salt solution in the stone, but also due to drying, or disconnection between the different components of the system. The ability to monitor the stone sample alone improves accuracy as well as minimises variables in the measurements.

The results of this study have corroborated the existing research concerning variables that affect impedance measurements on sandstone; porosity is not one of the main factors that determine the results. Neither is a variation in moisture content, until there is less than 20% wc within the pores. This is because as the pore system dries out a liquid film along the pore surfaces connects though the sample, keeping the electrical connection between electrodes constant. Only once the liquid film is disconnected (at saturations lower than 20% wc) does the impedance increase. The introduction of $1m\ NaCl$ solution (ca. 0.75g per sample) into the pore system decreases the impedance by two orders of magnitude compared to distilled water. The correlation between salt and impedance was clear: the more salt, the lower the impedance. The lowest concentration salt solution tested was the standard limit for intervention, at $0.2m\ NaCl$ (ca. 0.15g per sample). Even for this low concentration the impedance was measured at one and a half orders of magnitude less than distilled water. From this it is clear that impedance can be used to detect whether or not there is more salt than desirable in stone objects, in cases where there is a known baseline.

Four Clashach sandstone samples were saturated with $1m\ NaCl$ and treated with ED for 24h, 48h, 72h and 96h. When comparing the salt content at these intervals to the impedance, the data fits the curve found for salt and impedance previously found in this study. The inflection point for the graph is between 0.06g and 0.02g of $NaCl$, impedance is increased over three times the previous value. This shows how sensitive impedance is to very small amounts of salt content. Based on this data impedance can be used to monitor the desalination of stone in real time.

This study has identified three different phases of desalination. During the first 8h, impedance is increased quickly, from ca. 0.1kΩ to almost 1kΩ. Post-treatment destructive testing showed that 60% of salt is removed during the first 24h, and given that salt and impedance show a correlation, it is likely that most salt is removed during these 8h. After the initial rise in impedance, the impedance is at a stable magnitude 2-3 days, followed by another sharp increase towards the end of the treatment. Further studies are required to replicate these findings in other rock types, treatment rates and salt concentrations.

The application of ED will depend on the location, on the site/sample conditions, and especially outdoors will require some planning to prevent invasive measures. This is one of the most pressing concerns for future studies to address. Other studies should also investigate how different salts affect impedance measurements, as well as create a baseline matrix for a variation of stone types.

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Appendix 1 - Guide for ED experiments