New Double Electrode System for the Electrochemical Desalination of Building Stones

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New double electrode system for the electrochemical desalination of building stones

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Abstract:

The application of electrokinetic techniques for the mobilization and the removal of ions present in different porous materials, such as building construction materials, have shown high efficiency with respect to that reached with other techniques. However, some drawbacks related mainly with the mobilization efficiency of the ions of interest and with the integrity of the porous material due to the possible chemical and/or aesthetic damages have still to be overcome to take advantage of the full potentiality of these techniques. To overcome these limitations the present study evaluates the effectiveness of a new electrokinetic configuration based on the use of two electrodes per compartment that allow modulating the net amount of OH^- and H^+ groups produced at the electrodes' surface. This effectiveness was evaluated desalinating sandstone samples contaminated with different salts. The results indicate that the new configuration allowed: maintaining a high moisture content, both in poultices and stones, which allowed the treatment to work properly for longer time; to reach high percentages of reduction of all the ions present in the treated stones; to effectively buffer the pH variations due to the possibility of modulate the net amount of OH^- and H^+ groups produced.

Keywords: Electromigration, electroosmosis, desalination, sandstone, soluble salts, double electrode

1. Introduction

Electrokinetic techniques have shown high efficiency in the mobilization of ions present in porous materials and have been applied for that purpose in several fields, such as the extraction of heavy metals in contaminated soils (Jeon et al. 2015) (Ottosen et al. 2001, 2005) (Yeung and Gu 2011), the recovery of contaminants as the phosphorus present in sewage sludge (Guedes et al. 2014) (Ottosen, Kirkelund and Jensen, 2013) (Parés Viader

et al. 2015) (Sturm et al. 2010) or metals present in waste dumps (Hansen, Rojo and Ottosen 2012) (Idris, Inanc and Hassan 2004) (Pedersen, Ottosen and Villumsen 2005). The removal of soluble salts present in porous materials used in building construction such as concrete (Orellan, Escadeillas and Arliguie 2004) (Polder 1996) (Shan et al. 2016), bricks (Ottosen, Rörig-Dalgaard and Villumsen 2008) (Ottosen, and Rörig-Dalgaard 2009), ceramic (Ottosen, Ferreira and Christensen 2010) or ornamental rocks (granite (Feijoo et al. 2013, 2018a) (Feijoo, Ottosen and Pozo-Antonio 2015), sandstone (Feijoo et al. 2016) (Matyscak, Ottosen, and Rörig-Dalgaard 2014) (Ottosen and Christensen 2012), limestone (Ottosen, Christensen and Rörig-Dalgaard 2012)) represents also a very large domain of application. In this field (intervention of building materials), the efficiency showed by this technique in different porous materials (which can be consulted in the studies mentioned above) is higher than that achieved by other desalination techniques such as: immersion baths in water (Koob and Yee Ng 2000) (Unhruh 2001), use of crystallization inhibitors (Lubelli and van Hess 2007) (Rivas et al. 2017), application of poultices (Lubelli and van Hess 2010) (Lubelli, van Hess and De Clercq 2011) (Vergès-Belmin and Siedel 2005) or sacrificial mortars (Setina et al. 2009) (Husillos-Rodríguez et al. 2018), among others.

The operation of the electrokinetic techniques has two main limitations that affect the mobilization efficiency of the ions of interest:

1) The entrance into the medium to be treated of a high quantity of OH^- and H^+ formed at electrodes by water reduction and oxidation, respectively. These species are about one order of magnitude more mobile than the other ions (Ottosen et al. 2008) (Rörig-Dalgaard 2012) (Sa'id-Shawqi, Arya and Vassie 1998) which causes decreased current efficiency towards mobilization of the ions of interest (Castellote, Andrade and Alonso 2000) (Feijoo, Ottosen and Pozo-Antonio 2015) (Kamran et al. 2012) (Rörig-Dalgaard 2012).

2) The differential drying process that occurs in the vicinity of one of the electrodes, which restricts or hinders the flow of the electric current through the material, resulting in reduction of the operating time (Ottosen, Rörig-Dalgaard and Villumsen 2008) (Ottosen, Pedersen and Rörig-Dalgaard 2007) (Ottosen and Rörig-Dalgaard 2007). This fact, due to the establishment of an electroosmotic flux, hinders the contact between the current-driven electrode and the surrounding material. The direction of the electroosmotic flux depends on the surface charge of the pores network of the material through which the electric current flows (Asadi et al. 2013) (Ottosen et al. 2008). As the surface charge of most construction materials is negative, the electroosmotic flux tends to hydrate the material located at the cathode (Bertolini et al. 2009) (Franzoni 2014) (Franzoni, Bandini and Graziani 2014).

Desalination of porous materials used in construction, especially those used in monuments catalogued as cultural heritage, faces some limitations. One of them particularly relevant is the possibility of chemical alteration of rock forming minerals or chemical compounds present in construction materials because of their exposure to extreme pH values generated during the electrokinetic treatment. These extreme pH values (acidification and alkalization) occur at the vicinity of the electrodes (anode and cathode respectively) due to the water hydrolysis (Auras and Albertsen 2008) (Feijoo et al. 2013) (Feijoo, Ottosen and Pozo-Antonio 2015) (Ottosen et al. 2008) (Rörig-Dalgaard, Ottosen and Hansen 2012), according to Eq. 1 and Eq. 2.

A second limitation is the possibility of altering the aesthetic value of the materials due to color changes. These color changes are usually associated with changes in the oxidation

state of some chemical elements present in the materials composition, such as Fe^{2+} or Mn^{2+} , mainly in the vicinity of the anode (Auras and Albertsen 2008). Fe^{2+} and Mn^{2+} are stable in acidic media, but tend to oxidize at neutral to alkaline pH values.

In a previous study (Feijoo et al. 2018b) the effectiveness of a new electrokinetic setup based on the use of two electrodes at the anode, between which different potentials were applied was analyzed. This device, validated during the extraction of soluble salts from a sandstone, allowed the establishment of an electro-osmotic process at the anode that increased the duration of the conventional electrokinetic procedure (i.e. using a unique electrode at the cathode and at the anode). The double-anode setup improved also the pH buffering capacity at the anode and increased the effectiveness of the conventional desalination treatment due to reduction of the H^+ concentration in the vicinity of the stone. However, a high pH values were observed at the cathode which could limit the application of this setup in certain cases because:

- a) The treated material could be affected by alkaline pH values.
- b) The probable entrance of a higher fraction of OH^- ions in the material will reduce the effectiveness of the treatment.

The present study aims at evaluating the efficiency (in terms of percentage of removal of ions, in this case soluble salts) and the behavior (in terms of water content and pH buffering capacity) of a new electrokinetic configuration based on the use of two electrodes per compartment. The effectiveness of this new double electrode device is evaluated comparatively to a configuration with two electrodes only at the anode (the set up tested in (Feijoo et al. 2018b)) and to another configuration with two electrodes at the cathodic compartment. Different potentials will be applied between electrodes of the same compartments in all setups.

2. Materials and Methods

2.1. The porous material

An ashlar of sandstone extracted from the Kronborg castle located in Helsingor (Denmark) was used for this study; this castle was declared as a World Heritage Site by UNESCO in 2000.

The mineralogical and chemical composition and the main physical properties of the sandstone (accessible porosity of water, water absorption coefficient, capillary porosity, tortuosity, zeta potential...) are detailed in previous researches (Feijoo et al. 2016, 2017 and 2018b). Briefly, the most relevant characteristics of this rock are the following:

- 1) It is a very fine grained sandstone, composed mainly by subangular quartz grains (50–100 μm) cemented by kaolinite plates. The main major chemical elements are SiO_2 (95.07 %) and Al_2O_3 (3.26 %) with a low content of CaO (0.418 %), TiO_2 (0.323 %), K_2O (0.203 %), Fe_2O_3 (0.177 %) and Na_2O (0.15 %).
- 2) The accessible porosity to water is 13.24% and to mercury is 17.30%. This difference indicates that this rock has a certain pore volume hardly accessible to water.
- 3) The saturation degree by immersion is close to 100%, which indicates that the pore connectivity of this rock is high.
- 4) Most pores lie in the capillary range (80% of the pore volume), which corresponds to pores between 0.1-100 μm (Meng 1994), being its capillary porosity 11.47%.
- 5) The zeta potential value of this stone (i.e., the surface charge of its porous network) is negative (-24 mV); this negative charge will favor the transport of cations, as it occurs

for cation selective membranes (Tanaka 2007), so it is expected that the electroosmotic process will occur towards the cathode.

In this study 12 stone prisms of $6 \times 6 \times 3 \text{ cm}^3$ of this sandstone were used. In order to analyze the effectiveness of the electrokinetic technique to extract salts with different mobility, all the prisms were contaminated with a saline solution composed of 9.9% NaNO_3 , 6.6% NaCl and 0.66% CaSO_4 in weight. Before the contamination, the samples faces were marked in order to guarantee equal orientation during the contamination process and that the same parts of the rock were later compared throughout the study to calculate the extraction efficacy. The contamination process consisted in subjecting the stone prisms to periodic cycles (7 cycles in total) which consisted of 3 days of capillary absorption followed by 2 days of drying at room temperature. The face of the rock in contact with the saline solution was changed every cycle, in order to try to get a homogeneous distribution of the salts within the stones.

At the end of this contamination process, three of these stone prisms were used to determine the initial ion content, the reference values. For this purpose, the stone prisms were segmented into the 4 pieces previously labeled by hammer and chisel, weighed and crushed using a pulverizer ring mill; three representative samples of 10 g each were obtained for every crushed piece. Each sample of 10 g was stirred in 25 mL of distilled water during 24 h and filtered under vacuum through $0.45 \text{ }\mu\text{m}$ nitrocellulose filter, obtaining an aqueous extract per sample. In this aqueous extract, pH was measured (pH-meter BASIC20) and the Cl^- , SO_4^{2-} and NO_3^- contents were obtained by high resolution chromatography using a Dionex ICS-100 chromatograph.

The initial average ion content, in mg/g were: Cl^- : 1160.71 ± 56.77 ; SO_4^{2-} : 90.19 ± 7.57 ; NO_3^- : 2195.50 ± 113.53 . The low deviation between the ion content for the pieces of the

three reference stone prisms demonstrate that the salts are homogeneously distributed throughout the whole sample and also that the initial ion content is representative to the rest of the stone prisms.

The rest of the stone prisms (9 prisms) were desalinated using three different setups (3 prisms per setup) according to the procedures detailed in the next section.

2.2. Electrochemical setups. Description

Three different setups were evaluated. The first one is called in this study “DAC-S” (Double Anode and Cathode setup) and it has two electrodes per compartment, two at the cathode and two at the anode. The second setup evaluated is called “TE-A” (Two Electrode at the Anode) and it has two electrodes in the anodic compartment and only one electrode in the cathodic compartment (Fig. 1); this setup is similar to that evaluated in (Feijoo et al. 2018b). The third setup evaluated in this study is called “TE-C” (Two Electrodes at the Cathode) and it has two electrodes in the cathodic compartment and only one in the anodic compartment. As it can be seen in Fig. 1, the DAC-S setup results from merging of the other two setups, TE-A and TE-C.

INSERT FIGURE 1

The compartments containing two electrodes consist of two media separated by a cellulose filter. The media labeled in Fig. 1 M1 and M2 correspond to the anodic side, and M3 and M4 to the cathodic side. These media differ on the composition of the poultice filling each compartment, and on the potential established at the electrode hosted therein (Fig. 2).

INSERT FIGURE 2

The medium M1 is filled with a poultice (PA1) composed of cellulose and an electrolyte of citric acid and sodium citrate buffered at pH 6 in a weight ratio of 1:7.6. This composition was selected, as mentioned in (Feijoo et al. 2018b), because cellulose has a high liquid storage capacity but no pH buffering capacity, which would allow a large amount of H^+ ions to be generated in the vicinity of the electrode 1. In this electrode 1 a potential drop V_1 of 2V with respect to the electrode 2 was established by means the power supply 1. The electrode 1 was used only in the setups TE-A and DAC-S and was set at potential V_1+V_2 and $V_1+V_2+V_3$ respectively, depending on the setup used. Therefore, the electrode 1 can be considered, in these setups, as the effective anode.

A second medium (called M2) is filled with a poultice (PA2) composed of kaolin, calcium carbonate and citrate/citric acid electrolyte buffered at pH 6. The three components in a weight ratio 1:2:1.3 respectively. This composition is the same as the used in (Feijoo et al. 2018b). The addition of calcium carbonate is the conventional way in order to buffer the acid pH and it is based on the decomposition of calcium carbonate at acidic pH according to Eq. 3, followed by reaction of the carbonate ions with the H^+ generating CO_2 and H_2O (Eq. 4). In the PA2 poultice the electrode 2 was inserted, establishing a constant voltage V_2 of 10V using the power supply 2. In TE-A and DAC-S setups, the electrode 2 behaves as bipolar electrode because it acts as anode with respect to the electrode 3 and as cathode respect to the electrode 1. In TE-C setup, this electrode behaves as the effective anode.

These two media, M1 and M2, constitute the anodic compartment in the setups TE-A and DAC-S. In the setup TE-C, the anodic compartment was formed only by the medium M2.

In the cathodic compartment, another two media, M3 and M4, were used depending on the setup (Figs. 1 and 2). The M3 medium is placed close to the material to be treated, this medium was filled with a poultice (PC2) made of kaolin and citrate/citric acid electrolyte buffered at pH 6 in a weight ratio of 1.6:1. As mentioned in (Feijoo et al. 2018b), kaolin was selected by its ion exchange capacity, which allow to retain the OH^- ions generated in this compartment. In this medium, electrode 3 was inserted. In the setups TE-C and DAC-S a constant voltage of 1V was stablished using the power supply 3, whereas in the setup TE-A 0V potential was stablished. In consequence, this electrode can behave as bipolar electrode (in TE-C and DAC-S) or as effective cathode (in TE-A) depending on the setup used.

The other medium in the cathodic side, M4, was filled with a poultice (PC1) made of kaolin, calcium carbonate and citrate/citric acid electrolyte buffered at pH 5. This acidic pH value was selected in this case in order to favor the dissolution of calcium carbonate: the calcium ions released can react with the OH^- ions generated at the electrode surface, favoring in this way the OH^- immobilization via precipitation of $\text{Ca}(\text{OH})_2$ (Ottosen, Ferreira and Christensen 2010). In this medium, the electrode 4 was inserted and a voltage of 0V was established, behaving therefore as the effective cathode.

These two media, M3 and M4, constituted the cathode compartment in setups TE-C and DAC-S. While, in the setup TE-A, only the medium M3 formed the cathode compartment.

All the electrodes used were made of titanium-MMO mesh (titanium coated with mixed metal oxides) because of its inertness against oxidation reactions.

The stone prisms were wrapped with polyethylene film to hinder evaporation through the faces parallel to the current flux.

The application time of each setup lasted 16 days. Tests with each setup were performed in triplicate using for this purpose 3 stone prisms contaminated with the saline solution described above.

2.3. Operation of the setups

The three setups proposed in this study base their operation on the idea of bipolar electrodes, where a series of bars inserted in a medium are asymmetrically polarized when two external electrodes are connected to a power supply (Hansen, Rojo and Ottosen 2012) (Mavr et al. 2010). Due to these polarization processes one of the surfaces of the bars will act as the cathode of the positive electrode and the other surface will act as the anode of the negative electrode. However, unlike the setups proposed in this study, the use of bipolar electrodes does not allow to control the degree of polarization of the bars.

In the three setups, it is possible to regulate the variation of proton concentration $\Delta[H^+]$ generated at the surface of each electrode. This variation, according Faradys' law and Eq. 5-7, depends on the circulated charge and therefore on the current intensity and time.

$$\text{At electrode 1: } \Delta[H^+] = Q_1/F \quad w = I_1 t / F w \quad (5)$$

$$\text{At electrode 2: } \Delta[H^+] = Q_2/F \quad w = (I_2 - I_1) t / F w \quad (6)$$

$$\text{At electrode 3: } \Delta[H^+] = Q_3/F \quad w = (I_3 - I_2) t / F w \quad (7)$$

Being Q the circulating charge in C; F the Faraday's constant (96485 C/mol), w the volume of the compartment, I the circulating current in A and t the time elapsed in s.

Taking into account these equations, it is expected that in the setups with two electrodes hosted in the anodic compartment (TE-A and DAC-S), the following effects will occur at the electrode 2 (Fig. 3):

- Generation of water molecules due to the reaction of the generated H^+ , mainly at the electrode 1, and the OH^- generated at the electrode 2.
- Self-buffering capacity of the acidic pH at the anode because of the local OH^- production due to I_1 flow (Fig. 2).
- High desalination effectiveness due to the reduction of the H^+ amount that enter into the stone.
- Decreasing of the amount of Ca^{2+} released from the decomposition of the poultice PA2, which reduces the probability of clogging some of the pores of the stone by $Ca(OH)_2$ precipitation.

All these effects have already been described in a previous study (Feijoo et al. 2018b).

INSERT FIGURE 3

In the setups with two electrodes hosted in the cathodic compartment (TE-C and DAC-S), it is expected that the following effects occur at the electrode 3:

- Generation of water molecules due to the same reason mentioned above.
- Self-buffering capacity of the basic pH at the cathode due to the neutralization of the OH^- ions (generated at the electrode 4), with the H^+ ions generated at the electrode 3.
- High desalination effectiveness due to the reduction of the OH^- amount that enter into the stone. This reduction is increased using the poultice PC1 made of kaolin, calcium carbonate and electrolyte at pH 5 in the M4 medium. At this pH value it

is expected that the release of calcium occurs and consequently part of the calcium will fix the OH^- generated, forming $\text{Ca}(\text{OH})_2$.

Furthermore, from the previous equations it is possible to modulate the process and determine what current density it is necessary to apply, at each electrode, to reach a certain pH in each medium, for example to maintain the pH at 7 it would be necessary to apply the same current density at the three electrodes.

2.4. Methods for effectiveness evaluation

The total current intensity flowing into the circuit was periodically registered during the tests. Daily measurements were taken every 30 minutes during a time interval of 8 h by measuring the voltage drop that occurred in a resistance of $1\text{k}\Omega$ connected in series to the setup (Fig. 2). The current intensity flowing through each of the media, i.e. between the electrodes, was recorded directly from the respective power supply in the same time intervals. For the setups TE-A and TE-C two power supplies were employed, however in the setup DAC-S three power supplies were necessary (Fig. 2).

At the end of each test, each poultice was divided in three slices: A (the one closest to the anode), B (the intermediate portion) and C (the one closest to the cathode). Also, each sandstone prism was divided by chisel and hammer in the four parts previously marked: 1 and 2 (the closest to the anode) and 3 and 4 (the closest to the cathode) (Fig. 1).

In all of these poultice slices and sandstone parts, the following parameters were evaluated:

- a) The water content (in % g/g). This was aimed at evaluate whether an electroosmotic process could take place. This parameter was calculated as the

water content in the wet material with respect to the dry weight of the same material (poultice or stone). The dry weights were obtained after oven drying the poultice slices and stone parts at 105 °C for 24 hours, except the cellulose poultices which were dried at 50 °C for 3 days.

$$\text{Water content} = 100 * (\text{Weight of the wet material} - \text{Weight of the dry material}) / \text{Weight of the wet material}$$

The water content in the poultices was calculated before and after the treatment. For the stones the water content only was calculated at the end of the tests.

- b) The pH of the aqueous extract. The pH was determined after stirring of 10 g of each sample (poultices slices or stone parts) in 25 mL for 24 h, and further filtering through 0.45 µm mesh nitrocellulose filters. Three replicates were used for each fraction. For cellulose samples, 1 g instead 10 g was used.
- c) The ion content retained in each poultice and in the four stones parts. These measurements were performed by triplicate following the above described method. The efficacy of the desalination treatment (E%-ion), considered as the percentage of ion reduction achieved in the sandstone prisms, was calculated using the expression used in several researches (Feijoo et al. 2016, 2018a) (Lubelli, van Hess and De Clercq 2011) (Rivas et al. 2017):

$$E\%-ion_{1-4} = 100 * (\text{Initial ion content} - \text{Final ion content})_{1-4} / \text{Initial ion content}_{1-4}$$

3. Results and Discussion

3.1. Resistance and current intensity

Figure 4 shows the evolution of the total resistance and the total current intensity for the different setups evaluated in this study. There is a certain similarity between the

measurements recorded with the TE-A setup and with the DAC-S setup. In these two setups, the current intensity flowing through the stone prisms was higher than that recorded with the TE-C setup. Moreover, both records show similar trend with a nearly constant plateau during the first 200 hours of operation followed by a decreasing period of 200 more hours where the current decreases from 6 mA to approximately 2.5 mA. During the test, the total current intensity value obtained in the DAC-S setup was slightly higher than that obtained in the TE-A setup. The behavior of the resistance was, logically, the inverse.

The distinct behavior observed between the three setups applied to the same sandstone (especially between the DAC-S and TE-A with respect to TE-C) cannot be attributed to differences in material's porosity, since all the samples were contaminated under the same environmental conditions (T^a , RH) and following the same procedure, which caused a homogeneous distribution of the salts in the whole sample, as it was verified when the different parts of the three reference samples were analyzed. Alternate interpretations have to be proposed. One possibility lies on the differential current effectiveness when the salts are forced to migrate towards the electrodes. A greater mobilization of the ions implies a greater transport of electric current, measured as a lower resistance. In this sense, the current intensity registered indicates that the TE-A and especially DAC-S setups are more effective than the TE-C. Another possibility concerns the differential water content in the poultices located in the different media or in the sandstone prisms. A low moisture content in any of these materials can hinder and even prevent the current circulation. In this sense, the evolution of the current intensity during the test seems to indicate again that the TE-A and especially DAC-S setups are able to hinder the drying process to a greater extent than the TE-C. This drying process, taking into account the Z potential of this rock, occurs preferably in the anode zone. In this zone, as shown in

(Feijoo et al. 2018b), the use of 2 electrodes should allow the generation of water molecules that tend to hydrate the poultice PA2 and also to improve the contact between the electrode 2 and the PA2 poultice. In the TE-C setup, with a single electrode at the anode, the poultice PA2 tends to dry out and therefore the initially good contact between electrode-poultice tends to fade away. This fact was verified during the application of this setup, since periodic stirring up of electrode 2 was necessary to improve the ionic contact with the poultice. These actions were registered in the intensity and resistance records as marked fluctuations.

INSERT FIGURE 4

3.2. Water content

Table 1 shows the initial and final water content in the poultices and also the final water content in the sandstone prisms after application of the treatment according to the three setups tested.

The results obtained in the poultices are different depending on the setup used. With TE-A setup the highest reduction in water content occurs in the poultice PA1, composed of cellulose. This is due to the high initial water content of this poultice and also to the establishment of an electroosmotic process between electrode 1 and 2 which tends to increase water content at poultice PA2 while drying of poultice PA1, as demonstrated in a previous study (Feijoo et al. 2018b). The reduction of the water content achieved in the poultice PA2 was close to 12%, a value closer to the reduction achieved in the cathode poultice PC2 than that obtained in the anode poultice PA1.

INSERT TABLE 1

In the TE-C setup, the highest reduction in water content occurred in the poultice PC2 located in the medium M3. This is because the electrode 3 hosted in this medium acts as an anode with respect to the electrode 4 hosted in the medium M4, where a small percentage of reduction was observed. This result seems to indicate that an electroosmotic process took place between both electrodes that tends to hydrate the poultice PC1 and to dry the poultice PC2. The establishment of electroosmotic processes in clays is a well-known phenomenon (Grundl and Michalski 1996). At the anode, the water content that remains in the poultice PA2 was smaller than that remaining in the same poultice of the TE-A setup. The lower water content present in the poultices PA2 and PC2 (which were in contact with the stone), with respect to the water content of the same poultices in the TE-A setup, explains, as indicated in the previous section, why the amount of current flowing through the system was lower than that registered with the setup TE-A.

In the DAC-S setup, the highest reduction in water content in the anodic compartment occurred in the medium M1, as observed for the TE-A setup, while in the cathodic compartment the highest reduction in water occurred in the medium M3, as observed for the TE-C setup. This fact suggests that in both compartments a process of hydration of the poultices that hosted the electrodes with smaller potential (electrode 2 at the anode and electrode 4 at the cathode) took place. In the media closest to the stone prisms, M2 and M3, the percentages of reduction in water content were low and similar. These low water loss ensure that the wetting process of the stone prisms by the poultices can continue. The low percentage of reduction achieved in the poultice hosted in the medium M4 (effective cathode of the system) is a faithful reflection of the impact of the wetting process by electroosmosis.

Regarding the water content in the sandstones samples, after the 16 days of the test, the highest water content was achieved in the samples desalinated with the DAC-S setup and

the lowest with the TE-C setup. The water content that remained in the stones desalinated with the DAC-S setup was approximately 75% higher than that remained in the samples desalinated with the TE-C setup and approximately 60% higher than that remained in the samples desalinated with the TE-A setup.

As mentioned in the previous section, the highest water content, both in poultices (especially in those located close to the stone) and in the stone prisms, improves the contact electrode-poultice and in consequence favors the current flow lowering the resistance associated to the assembly (poultices and stone).

3.3. pH measurements

Figure 5 shows the pH average values measured in aqueous extracts of the poultice slices (A, B and C) hosted in the different media (M1, M2, M3 and M4) and of the stone parts (from 1 to 4).

INSERT FIGURE 5

Using the TE-A setup, the pH values reached in the medium M1 were extremely acid (below 2). This fact is due to the high quantity of H^+ ions generated in this medium and to the null buffering capacity of pH afforded by cellulose. In the medium M2 the pH increased, exceeding the value of 8. This increase was more noticeable in the slice C, in which the electrode 2 was located, where the pH value reached was above 10. These alkaline pH values, due to generation of OH^- ions at electrode 2 can be related with the unreacted $CaCO_3$ that remains in the PA2 poultice. The $CaCO_3$ present in the contact zone between the media M1 and M2 decomposes to acid pH values, releasing calcium that tends to fix the OH^- ions generated in the vicinity of the electrode 2 (Ottosen, Ferreira

and Christensen 2010). The pH of the sandstone prisms was alkaline after desalination, ranging from 9 (in the parts close to the anode), to 11 (in the parts close to the cathode medium M3). In the medium M3, high pH values were reached (slightly higher than 11). These results are similar to those obtained in (Feijoo et al. 2018b).

Regarding the TE-C setup, the results were different. At the anode (medium M2) the pH values did not exceed 8, being therefore lower than those reached with the TE-A setup. This fact could be related with the buffering process associated to the decomposition of the CaCO_3 present in the poultice PA2. Therefore the reduction in the CaCO_3 content of the poultice PA2 and the non-generation of OH^- ions in this compartment, since there is not any bipolar electrode, are the main reasons that can justify these pH values. With respect to the pH in the sandstone prisms, the parts closest to the anode (parts 1 and 2) showed pH values slightly lower than the pH values reached in the slice C of the poultice located in the medium M2 (ranging from 7.30 to 7.55), and similar to the characteristic pH of the untreated sandstone (7.15). The pH in the parts closest to the cathode (parts 3 and 4) showed high pH values (ranging from 8.20 to 9.45), which in any case were slightly lower than those reached in the cathode medium M3 (ranged from 9.70 to 10.80). At the cathode, the pH values were alkaline in both media, being slightly higher in the medium M4 (values close to 11). This fact is the expected considering that in this medium is located the electrode with zero potential (electrode 4), which acts as the true cathode of the setup.

Compared with the TE-A setup, the use of a second electrode in the cathode allow to reduce the amount of free OH^- ions that reach the vicinity of the stone (medium M3), and in consequence hinder the alkalization process that occurs at the cathode medium M3. This is due to: 1) the reaction of part of the OH^- ions with the H^+ ions generated on the surface of the electrode 3 and 2) the reaction between the calcium released in the setup

with the OH^- ions to produce $\text{Ca}(\text{OH})_2$. The calcium released that reacts with OH^- groups can come from: a) the decomposition of CaCO_3 present in the poultice PA2, during the buffering of the acid pH at the anode and the subsequent migration of calcium to the cathode and/or b) the decomposition of CaCO_3 present in the poultice PC1 located in the medium M4.

Using the DAC-S setup it was observed: 1) at the anode, acid pH values in the medium M1, which were not as extreme as those reached with the TE-A setup. This is because the potential difference between the electrode 1 hosted in this medium and the electrode 3 hosted in the medium M3 was smaller (12V in the TE-A setup, 11V in the TE-C setup). In the medium M2, the pH values (ranged from 9.40 to 10.90) were similar in some cases to those reached with the TE-A setup and higher than those reached with the TE-C setup, because there is less decomposition of the CaCO_3 present in the poultice PA2; 2) In sandstone prisms, the pH values were similar to those reached with the TE-C setup, below 8.7 in the area near the anode and below 10 in the area near the cathode. This is due to the lower entrance of OH^- ions inside the stone; 3) at the cathode, the behavior was similar to that recorded in the TE-C setup, alkaline pH values in both media, but higher values in the medium M4 than those reached in the medium M3, due to the reasons mentioned above.

3.4. Ion content in the poultice samples

Table 2 shows the average amount of the anions retained in the poultices of each medium, the total average amount retained in each compartment (anode and cathode) and also the total average amount extracted from the sandstone prisms.

In general, regardless of the setup, the anion content was higher at the anode than at the cathode and between setups the highest extraction was achieved with the DAC-S setup. The anion content in the anodic compartment was higher for the setups DAC-S and TE-A than for the TE-C setup. A similar amount was extracted in the former both cases although the highest anion content in the cathodic compartment was achieved using the TE-C setup, followed by the DAC-S setup.

The greatest amount of ions mobilized were nitrates, followed by chlorides and to a lesser extent sulfates. This fact is related to the initial ion content of the sandstone prisms (content that is indicated in section 2.1).

INSERT TABLE 2

Analyzing each of the setups independently, we can see that:

- 1) Using the TE-A setup, most of the anions were mobilized towards the anode (more than 98% of the total), favored to a large extent by the generation of water molecules in this compartment that tends to reduce the speed of drying of the poultices PA1 and PA2, as it happened in (Feijoo et al. 2018b). Within the anode compartment, the amount retained in media 1 and 2 is practically similar in terms of chloride and nitrate. However, with respect to sulfate the results seem to indicate that the mobilization rate of this ion towards electrode 1 (effective anode of the setup) is slower. At the time of stopping the treatment the ratio of sulfate content in the medium M1 with respect to the medium M2 is very low.

The low anionic content present in the cathodic compartment can be related to diffusive and advective processes that also take place during the application of this type of treatments (Ottosen et al. 2008).

- 2) Using the TE-C setup, the differences between the anion mobilized towards the anode and that mobilized towards the cathode decrease. With this setup, the total amount of anions mobilized towards the anode was about 65%. Between the cathode media (M3 and M4), almost all of the anions were retained in the medium M3. This fact may be related with the preferential drying of the anode poultice PA2 due to the establishment of an electroosmotic process. When drying of this poultice occurs, the contact between the electrode 2 and the poultice PA2 begins to worsen, which affects the current flow. During this process, the importance of the electrode 3 as an anode increases, causing a mobilization of part of the anions, present in the sandstone prisms and in the medium M4, towards the poultice PC1 located in the medium M3.
- 3) Using the DAC-S setup, most of the anions were mobilized towards the anode (90% of the total), as occurred with the TE-A setup. This great mobilization was achieved due to the fact that the use of the two electrodes, in the anodic compartment, allowed to maintain a certain degree of humidity during a longer period of time. However, the DAC-S setup allowed to increase the amount of anions mobilized towards the cathode (10% of the total). This result could be related to the potential applied in the electrode 3 that would be responsible for the high amount retained in the cathode medium M3.

3.5. Ion content in the stone samples

Figure 6 shows the average effectiveness percentages of the anion extraction (chloride, nitrate and sulfate) in the four parts in which each stone sample was divided.

In general, the highest efficacy (E%-ion) in the different parts of the stone prisms were achieved with the application of the DAC-S setup. The different efficacy achieved between the setups was more pronounced in the case of chloride and nitrate and, to a

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3 lesser extent, in the case of sulfate. The lowest efficacy were obtained in most cases with
4 the TE-C setup. This fact seems to be related with the drying of the poultices, mainly
5 those located at the anode, and with the drying of the stone samples. In both cases, the
6 drying of these materials hinders the current flow and therefore the mobilization of the
7 anions.
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15 Despite the differences detected between setups, the desalination efficacy reached
16 throughout the sandstone prisms have been high, reaching in almost all cases extraction
17 percentages above 80%. This high effectiveness allows to classify the setups DAC-S and
18 TE-A as desalination treatments as of very high efficiency, and the TE-C as a treatment
19 of high efficiency, according to the classification established by (Zezza 2009).
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28 INSERT FIGURE 6
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31 In the case of the TE-A setup, the highest desalination levels, regardless of the anion,
32 were obtained in the stone parts closest to the cathode (parts 3 and 4). This is due to the
33 fact that, during the desalination process, the anions are mobilized from the cathode
34 towards the anode, leaving a higher quantity of anions in this part of the stone (parts 1
35 and 2). The extraction percentages of chloride and nitrate were similar (approximately
36 92.5% in the anode area and approximately 95% in the cathode area). In the case of
37 sulfate, the average efficacy was 90% in the anode area and 94% approximately in the
38 cathode area.
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50 Applying the TE-C a higher difference was observed between the efficacies reached in
51 the anode area (lower than 90%) and the cathode area (higher than 90%). This fact can be
52 related with the drying that takes place in the poultice of the anode, which hinders the
53 mobilization and subsequent exit of the anions that accumulate in the stone parts 1 and 2
54 (anode areas). The extraction percentages of chloride and sulfate were similar
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(approximately 85% in the anode area and approximately 93% in the cathode area) and higher than those achieved in the extraction of nitrates.

Using the DAC-S setup, the efficacy reached for each anion throughout the entire stone prisms was similar. These extraction percentages were very high in the case of chloride and nitrate (99%) and somewhat lower in the case of sulfate (approximately 94%). These results indicate that the application of the DAC-S setup allows, in the same period of time as the other two setups, to reach higher and more homogeneous desalination effectiveness.

Everything commented above, regarding salt distribution into the stones and the final ion content that remain in each of the stone samples after desalination with each setup, agrees with the data provided in Table 3 in which it is appreciated that: 1) the DAC-S was the setup that allowed to reduce the ionic content to a greater extent, leaving a low anion content in the stone samples and 2) unlike what happens with the TE-A and the TE-C, the final ion content in the samples desalinated with the DAC-S setup was similar throughout the entire sample.

INSERT TABLE 3

Conclusions

The main conclusions derived from this study are:

- The DAC-S setup allows maintaining a high water content in the rock and the poultices (both compartments) which allows to maintain a good ionic contact electrode-poultice-stone.
- The high water content afforded by the DAC-S setup allows maintaining higher operation currents, which increases ion mobilization.

- The DAC-S setup as well as the TE-C setup allow maintaining the pH of the rocks in the natural value, which minimizes chemical alteration. The cathode electrodes are the main responsible for this action.
- The three setups, and specially the DAC-S setup, allow to reach high percentages of ion extraction. The residual ion concentration remaining in the rock is symmetrical (anode and cathode sides) for the DAC-S setup while for the two other setups this symmetry does not exists and the results present some degree of scatter. Ion mobilization is then more homogeneous and efficient with the DAC-S setup.

It would be interesting evaluate in future researches, taking into account both the results achieved in this research -which confirm the suitability of the new setup- and the equations that modulate the system, if the application of equal current densities at the three electrodes will allow to desalinate any material keeping the pH of the different media in 7. This would allow to reduce the amount of calcium carbonate used and not have to use a buffer electrolyte which could cause color changes.

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FIGURE CAPTIONS

Figure 1. Scheme of the different setups evaluated in this study: DAC-S (which comprises two electrodes at the cathodic and at the anodic compartments) and TE-A and TE-C setups. Four media are distinguished (M1 and M2 in the anode, and M3 and M4 in the cathode) which are filled with different poultices (PA1, PA2, PC1, PC2) in which the electrodes are inserted. DAC-S setup comprises the four media, TE-A setup comprises M1, M2 and M3 and TE-C setup comprises M2, M3 and M4 media. It is also shown the different poultice slices (A, B,C) and the different parts of the stone samples (1, 2, 3 and 4) in which the materials are divided for the subsequent analyses. The blue lines indicate the site where the cellulose filters are located.

Figure 2. Scheme of the different electric circuits evaluated in this study. The dashed lines show the addition necessary to apply the different setups evaluated, i.e. TE-A: media 1, 2 and 3; TE-C: media 2, 3 and 4; DAC-S: all the media. The scheme also shows the power supplies, the electrodes located in each compartment, the variable resistances (which correspond to the resistance of the stone and poultices) and a fix resistance of 1 k Ω , in which the current intensity is registered. All of the elements connected in series.

Figure 3. Operation diagrams for the different setups evaluated in this study. a) TE-A, b) TE-C, c) DAC-S.

Figure 4. Average measurements of the total resistance (in k Ω) and the total current intensity (in mA) that flows through the sandstone samples during the application of each setup.

Figure 5. pH measurements registered in the different parts that make up each setup (poultices slices and stone parts).

Figure 6. Average efficacy percentage (n= 3 stone samples per setup) of Cl^- (a), NO_3^- (b) and SO_4^{2-} , reached in the parts in which the stone samples were divided (parts 1 and 2 closest to the anode and 3 and 4 closest to the cathode).

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188x126mm (150 x 150 DPI)

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312x107mm (72 x 72 DPI)

a) TE-A

b) TE-C

c) DAC-S

Figure 3. Operation diagrams for the different setups evaluated in this study. a) TE-A, b) TE-C, c) DAC-S.

150x195mm (150 x 150 DPI)

Figure 4. Average measurements of the total resistance (in k Ω) and the total current intensity (in mA) that flows through the sandstone samples during the application of each setup.

150x187mm (126 x 126 DPI)

Figure 5. pH measurements registered in the different parts that make up each setup (poultices slices and stone parts).

175x97mm (150 x 150 DPI)

Figure 6. Average efficacy percentage ($n = 3$ stone samples per setup) of Cl^- (a), NO_3^- (b) and SO_4^{2-} , reached in the parts in which the stone samples were divided (parts 1 and 2 closest to the anode and 3 and 4 closest to the cathode).

98x190mm (150 x 150 DPI)

Table 1. The average value and standard deviation of the water content (in % g/g) of the poultices used in each medium, before and after the desalination tests, and of the sandstone samples desalinated with each of the setups evaluated, at the end of the treatments. The reduction of the water content of the poultices (in %) is also shown.

		Water Content in the poultice (%)		
Setup	Medium/Poultice	Initial	Final	Reduction (%)
TE-A	M1/PA1	579.35±8.15	397.75±5.98	31.32±0.23
	M2/PA2	41.08±0.28	36.23±0.76	11.80±0.38
	M3/PC2	58.78±0.38	53.76±0.42	8.35±2.15
		Initial	Final	Reduction (%)
TE-C	M2/PA2	41.08±0.28	29.93±0.27	27.38±0.33
	M3/PC2	58.78±0.38	35.19±2.88	40.12±4.90
	M4/PC1	41.83±0.11	31.28±1.80	25.21±4.30
		Initial	Final	Reduction (%)
DAC-S	M1/PA1	579.35±8.15	259.25±4.15	55.25±0.72
	M2/PA2	41.08±0.28	33.06±0.01	19.53±0.34
	M3/PC2	58.78±0.38	47.50±1.47	19.18±2.51
	M4/PC1	41.83±0.11	40.37±0.51	3.92±0.61
Final water Content in the stone samples (%)		TE-A	TE-C	DAC-S
		3.13±0.18	2.83±0.23	4.99±0.01

Table 2: Average amount (n=3 sandstone prisms per setup) of Cl^- , NO_3^- and SO_4^{2-} in mg retained in the different media (from M1 to M4) that constitute each setup (TE-A, TE-C and DAC-S). Total average amount retained in each compartment (Anode=M1+M2 and Cathode= M3+M4). Total content extracted from the stone samples, i.e. the sum of the anode and cathode.

Set up	Ion	Ion content in each medium (mg/medium)				Total Anode (M1+M2)	Total Cathode (M3+M4)	Total
		M1	M2	M3	M4			
TE-A								
	Cl ⁻	421.55±55.51	580.26±42.51	20.28±0.73	-	1001.81±13.00	20.28±0.73	1022.09±12.27
	NO ₃ ⁻	972.00±56.57	1065.84±1.71	9.76±2.92	-	2037.84±58.28	9.76±2.92	2047.60±55.36
	SO ₄ ²⁻	18.81±3.94	52.70±3.18	8.68±1.52	-	71.51±7.12	8.68±1.52	80.19±5.60
TE-C								
	Cl ⁻	-	627.81±54.00	313.98±15.58	8.14±2.65	627.81±54.00	322.13±12.93	949.93±66.93
	NO ₃ ⁻	-	1125.89±42.27	595.84±225.4	13.14±12.75	1125.89±42.27	608.98±213.60	1734.87±307.58
	SO ₄ ²⁻	-	43.07±6.66	29.18±7.32	5.81±2.35	43.07±6.66	34.98±9.67	78.05±3.01
DAC-S								
	Cl ⁻	421.00±22.63	620.01±42.26	103.03±31.37	11.91±1.68	1041.01±18.37	114.94±33.06	1155.95±51.43
	NO ₃ ⁻	890.10±11.81	1134.23±80.32	187.42±15.57	17.18±2.17	2024.33±68.51	204.60±17.75	2228.93±86.26
	SO ₄ ²⁻	13.62±2.29	59.99±4.33	13.11±2.67	3.21±0.69	73.61±2.05	16.32±3.36	89.93±5.41

Table 3. Final average anion content and standard deviation (n = 3 stone samples per setup) of Cl⁻, NO₃⁻ and SO₄²⁻ (in mg/g) retained in the parts in which the stone samples were divided (parts 1 and 2 close to the anode and 3 and 4 close to the cathode) after the desalination treatment with each setup (TE-A, TE-C and DAC-S). The total average amount of each anion (in mg/g) retained in samples desalinated with each setup is also shown.

Setup	Ion	Part of the stone sample				Average
		1	2	3	4	
TE-A	Cl ⁻	19.38±2.43	12.54±1.54	10.32±1.69	11.82±4.87	13.51±4.34
	NO ₃ ⁻	21.71±4.39	17.14±0.27	13.98±7.58	15.45±2.90	17.07±4.67
	SO ₄ ²⁻	2.25±1.12	1.33±0.11	1.11±0.13	0.97±0.48	1.41±0.71
TE-C	Cl ⁻	33.26±14.53	28.72±11.21	14.50±7.76	25.68±3.54	25.54±10.64
	NO ₃ ⁻	83.25±37.66	70.93±31.12	37.00±20.23	78.95±25.27	67.53±29.47
	SO ₄ ²⁻	2.49±0.82	1.90±0.72	1.35±0.57	2.20±0.45	1.98±0.67
DAC-S	Cl ⁻	1.38±0.15	2.12±0.16	2.02±0.60	2.20±0.77	1.93±0.51
	NO ₃ ⁻	2.42±0.62	3.23±0.26	3.80±0.81	4.19±1.11	3.41±0.92
	SO ₄ ²⁻	1.48±0.11	0.85±0.46	0.85±0.34	0.88±0.35	1.02±0.38