

Salt extraction of limestone by means of electrophoresis: some results on type of contact material and electrode position

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Abstract

This paper describes some results of salt extraction by means of electrophoresis on limestone contaminated with two types of salts: NaCl and Na₂SO₄. Limestone plates in various dimensions have been tested. The electrophoresis is evaluated in terms of the measured current during the electrophoresis process and the remaining amount of salts in the samples, determined by conductivity measurements of the water extract. Three different contact materials have been tested: cotton, cellulose fibers and a mixture consisting of calcite powder and cellulose fibers. Results have shown that the last is the most efficient one. Two different electrode configurations have been tested on one type of the limestone plates. Results have shown that salts are removed from zones not necessarily positioned right between or physically in contact with the electrodes. There are indications that a better efficiency is obtained in case the electrodes are positioned on opposite sides, compared to an electrode-layout by which the electrodes are on the same side of the sample. It seems that the efficiency of the electrophoresis does not depend on the size of the electrodes, as long as the contact material is spread over the entire surface of the sample to be salt extracted.

Keywords: electrophoresis, limestone, contact material, sodium chloride, sodium sulphate

1 Introduction

Moisture and salt contamination is a major cause of degradation to historic building materials, in the form of aesthetic or mechanical damage. In Belgium, impermeable or salt resistant materials are quite often used in practice; interventions that have a tendency of hiding the salt problem instead of solving it and hence as such not contributing to a sustainable management of our built heritage. An alternative approach attempts to extract salts through poulticing or electrophoresis.

During electrophoresis, a wet sample contaminated with salts is subjected to a direct current enabling ions to migrate to the oppositely charged electrode where they are stored in the contact material. In case of sodium salts, sodium hydroxide is formed at the cathode or negatively charged electrode [1]. An alkaline environment as such is not damaging a limestone. At the positively charged anode, water is transformed into oxygen and hydrogen ions. Chlorides form chlorine gas or combine with hydrogen ions to form hydrochloric acid. Sulfates present in solution will similarly combine with the hydrogen ions and form sulfuric acid. An acidic environment can chemically attack the calcium carbonate of limestone and hence cause damage to it.

This paper describes some results of salt extraction by means of electrophoresis on limestone contaminated with two types of salts: NaCl and Na₂SO₄. Tested parameters are the type of contact material and the position of the electrode. Two types of limestone plates, more precisely 15x15x4 cm and 45x45x4 cm, are tested using a similar electrode having a size of 15x15 cm. Concerning the bigger plates, two different electrode configurations are tested: in the middle and at opposite sides of the plate on one hand and in the middle at the left and right and same side of the plate. The efficiency of the electrophoresis is expressed in terms of the measured current during the electrophoresis process and the remaining amount of salts. For the last, samples are crushed and poured into distilled water that is submitted to conductivity measurements. Three different contact materials are tested: cotton, cellulose fibers and a mixture consisting of calcite powder and cellulose fibers.

2 Materials

2.1 Substrates

Two types of limestone were tested in this investigation: Savonnières and Euville limestone, being respectively a semi-coarse oölitic and a coarse crinoidic French limestone. Savonnières limestone is characterized by a porosity accessible to water, determined by immersing dry samples in

demineralized water for 48 h, of 9.2 % while that of the Euville stone is 3.9 %. The limestones were cut into plates (15x15x4 cm or 45x45x4 cm).

Samples are dried at 105 °C till constant weight (difference between two weighings is less than 0.1 %).

2.2 Moisture and salt contamination

Limestone plates of 15x15x4 cm are contaminated with a saturated sodium chloride (NaCl) or sodium sulfate (Na_2SO_4) solution. The bigger plates are only contaminated with a saturated NaCl solution. The dry samples are poured into a saturated solution, containing or 369 g NaCl or 172 g Na_2SO_4 per liter water, during 48 hours. After that, the surfaces are made surface dry using a moistened cotton and the samples are weighed to determine their moisture and salt content. Prior to the electrophoresis, the samples contaminated with a saturated salt solution are covered with a plastic foil during 1 week to assure a homogeneous distribution of moisture and salt.

2.3 Contact materials – overview of samples

Three types of contact materials were included in this investigation: cotton, calcite powder and a mixture of cellulose and calcite powder. The choice of calcite powder is based on the research results obtained by L. Ottosen et al [2,3,4] in which a calcium carbonate rich clay was used as contact material. The calcite neutralizes the acids formed at the anode preventing a chemical damage of the lime substrate subjected to electrophoresis. Clay was not included in our research for its dense structure. It is supposed that calcite powder, characterized by a more open structure, will stimulate the evacuation of formed gaseous compounds, such as Cl_2 , O_2 and H_2 .

In case of calcite and calcite/cellulose, water is added to obtain a workable paste-like material and to assure a good contact with the limestone sample surface and the electrode. The paste-like contact material is added at a thickness of 1 cm. The cotton is also wetted prior to its attachment to the limestone plate samples. For plate samples of 45x45x4 cm, only a calcite/cellulose mixture is tested as contact material.

An overview of the samples is given in table 1.

2.4 Electrodes - electrophoresis

Results obtained during previous investigations have shown that stainless steel, copper as well as graphite net-electrodes got severely damaged during the electrophoresis process [5]. Hence, for present research plate graphite electrodes (15x15 cm) were selected for their good resistance in

an acidic and alkaline environment, low cost and easy availability. They are linked to the power supply by means of a titanium nut.

For the electrophoresis procedure, the ensemble, consisting of salt contaminated limestone plates, contact material and electrode, is protected by means of a plastic foil to minimize the evaporation of water. Little holes in the plastic foil enable the evaporation of formed gaseous compounds. In case of the 15x15x4 cm sized plate, the ensemble is kept together by means of a clip (figure 1). For the limestone plates of 45x45x4 cm, two different electrode configurations are tested: in the middle and at opposite sides of the plate on one hand and in the middle at the left and the right and same side of the plate (45x45 cm). The calcite/cellulose mixture is applied at a thickness of 1 cm on the complete surface (45x45 cm) of both opposite sides for the first configuration and on one side for the second configuration. The electrodes positioned in the middle of the opposite sides (first configuration) are kept in place using a wooden panel on both sides held together by means of screws (figure 2). A plastic plate between the wooden panel and the contact material serves as protection for the underlying contact material. For the second configuration, the electrodes are fixed similar to the small plate samples.

A voltage of 10 V was applied during 1 week. The current is measured continuously to follow up the electrophoresis process.



Figure 1: Setup for the limestone plates of 15x15x4 cm

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Table 1: overview of the samples

Salt / contact material	cotton	calcite	calcite/cellulose
	Sample code		
Euville limestone (15x15x4 cm), electrodes (15x15cm) on opposite side			
NaCl	E1'	E2	E3
Na ₂ SO ₄	E4'	E5	E6
Savonnières limestone (15x15x4 cm), electrodes (15x15cm) on opposite side			
NaCl	S1'	S2	S3
Na ₂ SO ₄	S4'	S5	S6
Euville limestone (45x45x4 cm), electrodes (15x15cm) on opposite side			
NaCl	-	-	EX
Euville limestone (45x45x4 cm), electrodes (15x15cm) on same side			
NaCl	-	-	E
Savonnières limestone (45x45x4 cm), electrodes (15x15cm) on opposite side			
NaCl	-	-	SX
Savonnières limestone (45x45x4 cm), electrodes (15x15cm) on same side			
NaCl	-	-	S



Figure 2: The electrodes, applied in the middle of the opposite sides of limestone plates of 45x45x4 cm, are kept in place using a wooden panel on both sides and positioned by means of screws. A plastic plate applied between the wooden panel and the contact material serves as protection for the contact material underneath it.

2.5 Electrophoresis efficiency

After 1 week electrophoresis, the contact material is removed from the limestone samples which are dried at 105 °C till constant weight. After that, samples of 15x15x4 cm are entirely crushed and poured into 4 l of demineralized water to determine the remaining amount of salts through conductivity [5]. Limestone plates of 45x45x4 cm are divided in 9 equal parts of 15x15x4 cm that are further treated similarly. Conductivity results are interpreted based on a calibration procedure using aqueous solutions with known NaCl or Na₂SO₄ concentrations.

3 Results and discussion

3.1 Plates of 15x15x4 cm

Figures 3 and 4 present by means of illustration the evolution of the measured current during the electrophoresis of respectively Euville limestone contaminated with a saturated Na₂SO₄ solution and Savonnières limestone with a saturated NaCl solution, for the three types of contact materials. From both figures, it can be noticed that the highest current is obtained in case calcite/cellulose mixtures are used as contact

material, while generally the lowest in case of calcite. Similar results were obtained for Euville limestone saturated with NaCl and Savonnières limestone with a Na_2SO_4 solution (figure 5). By comparing the results presented in figures 4 and 5, it can generally be noticed that a higher current is measured in case of a contamination with NaCl compared to one with Na_2SO_4 . This can be explained by a higher mobility of chlorides compared to sulfates. Higher currents are measured for the Savonnières limestone compared to the Euville limestone (figures 5 and 3 respectively).

The efficiency of the salt removal by means of electrophoresis is presented in table 2.

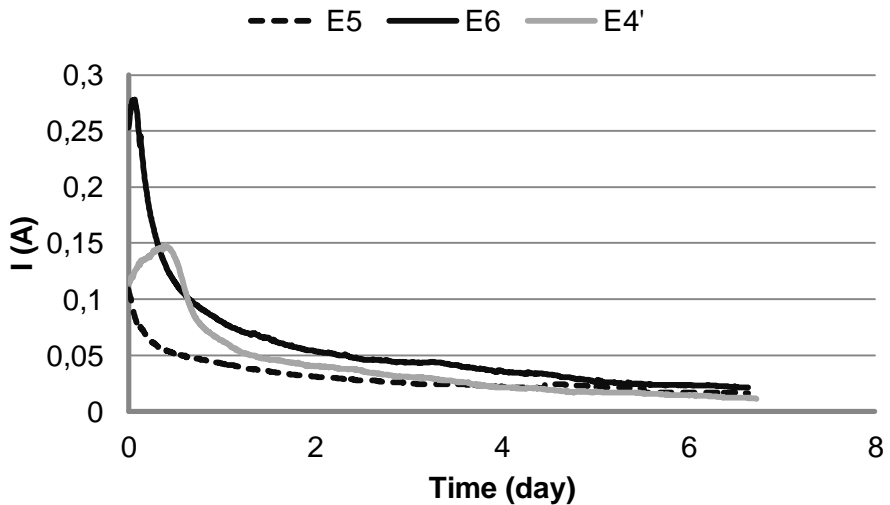


Figure 3: Evolution of the current during electrophoresis of Euville stone plates of 15x15x4 cm contaminated with a saturated Na_2SO_4 solution using cotton (E4'), calcite (E5) or a mixture of calcite and cellulose (E6) as contact material.

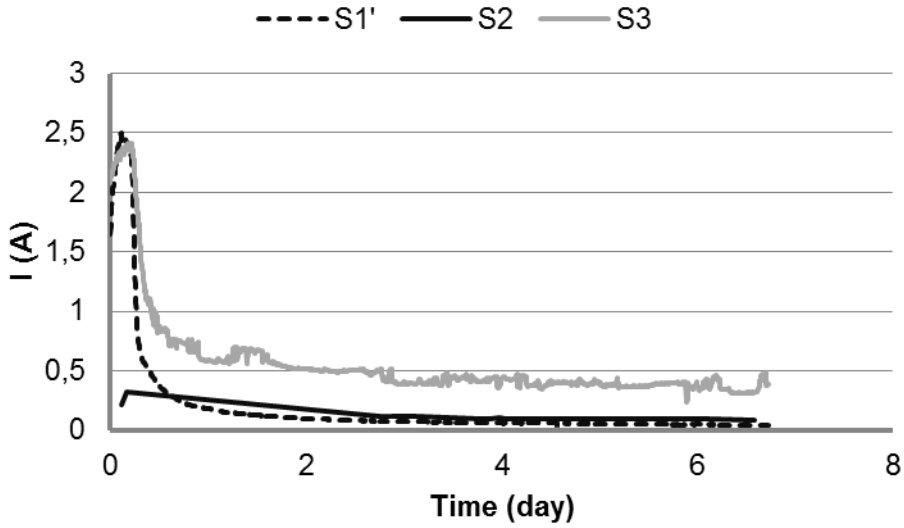


Figure 4: Evolution of the current during electrophoresis of Savonnières stone plates of 15x15x4 cm contaminated with a saturated NaCl solution using cotton (S1'), calcite (S2) or a mixture of calcite and cellulose (S3) as contact material.

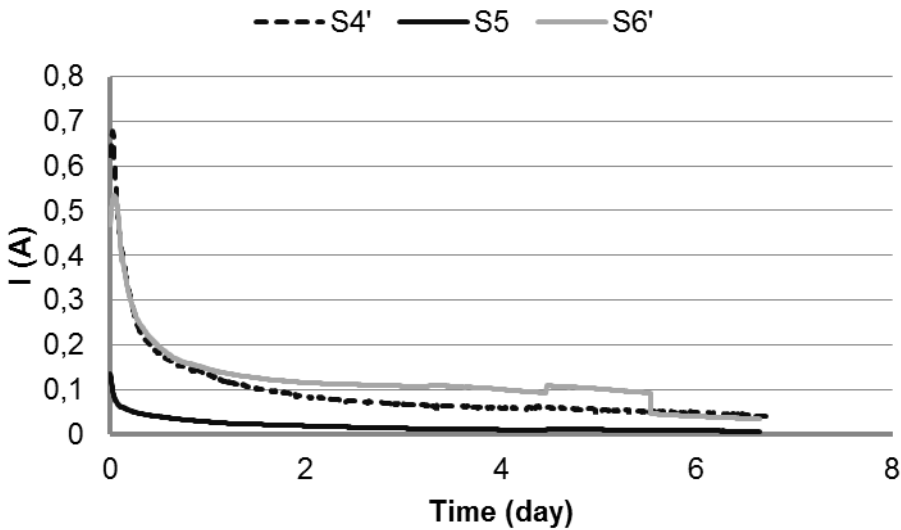


Figure 5: Evolution of the current during electrophoresis of Savonnières stone plates of 15x15x4 cm contaminated with a saturated Na₂SO₄ solution using cotton (S4'), calcite (S5) or a mixture of calcite and cellulose (S6) as contact material.

Table 2: efficiency (%) of salt removal by means of electrophoresis using three kinds of contact materials for Savonnières and Euville limestone plates of 15x15x4 cm contaminated with a saturated NaCl or Na₂SO₄ solution.

salt	cotton		calcite		calcite/cellulose	
	Sample code	Efficiency (%)	Sample code	Efficiency (%)	Sample code	Efficiency (%)
Euville limestone						
NaCl	E1'	52.3	E2	41.7	E3	49.4
Na ₂ SO ₄	E4'	31.2	E5	34.5	E6	52.9
Savonnières limestone						
NaCl	S1'	31.2	S2	35.7	S3	40.2
Na ₂ SO ₄	S4'	18.3	S5	12.7	S6	53.5

The three main conclusions are:

- The results in table 2 show that generally the highest efficiency is obtained for a calcite/cellulose mixture as contact material. This corresponds well with the higher current obtained with this poultice type (figures 3-5)
- Except for the last type of contact material, a higher removal is measured for Euville and Savonnières limestone contaminated with NaCl compared to Na₂SO₄, despite its higher solubility, and hence higher absolute initial content after contamination with a saturated solution. In addition, precipitation of Ca(SO₄) may have immobilized the sulphate. Formation of gypsum has indeed been observed in other research [6].
- Comparing the influence of the type of limestone, better results are noticed for the coarser Euville limestone. It should be remarked here that this crinoidic limestone contained, in absolute values, initially less salts as its porosity accessible to water is remarkably lower (3.9%) compared to the Savonnières limestone (9.2%). This finding again corresponds to the higher current in the Savonnières limestone.

3.2 Plates of 45x45x4 cm

In the test procedure using plates of 15x15x4 cm, the plate electrode covers completely both opposite sides (15x15 cm). It should be more practical to reduce the size of the plate compared to the surface subject of a salt extraction procedure. For on-site applications, it's rather illogic to cover a complete façade surface to be salt extracted with electrodes. It might be more advantageous to apply a series of electrodes at a fixed distance between each other. As a first approach to evaluate to what distance salts can be extracted by means of electrophoresis, preliminary tests are carried out on bigger limestone plates (45x45x4 cm) using the same plate electrodes as tested on the little plates and calcite/cellulose fibers as contact material. Two different electrode configurations are tested: in the middle and at opposite sides (45x45 cm) of the plate (1) and in the middle at the left and the right and same side of the plate (2). The second configuration mimics a situation where a wall is only accessible from one side, as is the case for cellars, or in the case of presence of constructions on the other side of the wall. One could think of a frame by which the electrodes are positioned as vertical forms on one side of a wall and at a certain distance, as was investigated by Ottosen et al [4]. A crucial parameter for such type of application is related to the distance between the electrodes, which should preferably be as high as possible to reduce eventual (mechanical) damage associated with the fixation of the electrodes to the wall.

Figure 6 illustrates the evolution of the measured current for Euville and Savonnières limestone contaminated with a saturated NaCl solution during the electrophoresis according to the two test configurations.

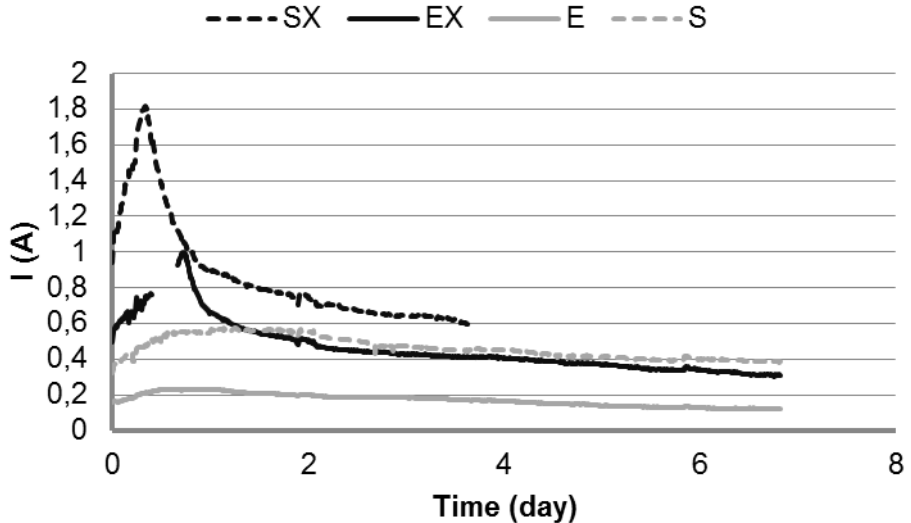


Figure 6: current measured during electrophoresis of Euville (E) and Savonnières (S) limestone plates of 45x45x4 cm contaminated with a saturated NaCl solution according to two configurations (EX and SX refer to the configuration by which the electrodes are positioned in the middle at both and opposite sides of the limestone plate; E and S refer to the configuration by which the electrodes are positioned in the middle at the left and the right and same side of the plate).

The electrophoresis by which the electrodes are applied in the middle of the opposite sides (SX and EX), results in a higher current compared to a procedure by which the electrodes are positioned on the same side (S and E), which is explained by a shorter distance in between, respectively 4 and 15 cm. If the resistance in the stone is considered homogeneous, a longer distance between the electrodes will result in a higher distance and a lower current (as the voltage is kept constant in these experiments). Similar as for the smaller plates, a higher current is measured for Savonnières plates than for Euville ones.

Results of extraction efficiency, based on conductivity measurements, are presented in tables 3 and 4. In order to calculate the efficiency of the electrophoresis, the assumption is made that initially the salts are distributed homogeneously over the volume of the sample.

Table 3: electrophoresis efficiency (%) of 9 equal parts (15x15x4 cm) of Euville (EX) and Savonnières (SX) limestone plates (45x45x4 cm) contaminated with a saturated NaCl solution and subjected to electrophoresis. The electrodes were applied in the middle of the opposite sides. The electrode position is marked in grey.

position	EX			SX		
	Left	Middle	Right	Left	Middle	Right
Top	60,8	65,7	58,8	52,0	57,2	47,9
Middle	63,4	66,1	62,0	56,1	53,1	54,8
Bottom	64,9	65,4	59,9	53,4	57,1	49,1
Global average	63			53		

Table 4: electrophoresis efficiency (%) of 9 equal parts (15x15x4 cm) of Euville (E) and Savonnières (S) limestone plates (45x45x4 cm) contaminated with a saturated NaCl solution and subjected to electrophoresis. The electrodes were applied in the middle at the left and the right and same side of the plate. Their position is marked in grey.

position	E			S		
	Left	Middle	Right	Left	Middle	Right
Top	35,1	42,8	39,8	27,2	39,1	24,5
Middle	42,2	57,4	49,9	27,8	45,9	29,4
Bottom	40,2	52,3	46,9	36,0	39,5	30,2
Global average	45			33		

The results presented in the tables 3 and 4 illustrate that a higher efficiency is obtained in case the electrodes are applied at opposite sides of the plate at a distance of 4 cm than at the same side at a distance of 15 cm between each other, corresponding to the higher current. With respect

to the first configuration (table 3), the difference in salt extraction efficiency between the different parts of the same limestone plate is rather small and unsystematic. An expected higher efficiency for the limestone part right between the electrodes is only obtained in case of the Euville limestone. For electrode configuration 2 (table 4), the highest efficiency is obtained for the limestone part right between both electrodes, hence the middle part of the plate. Nevertheless, it is still lower than the average efficiency obtained for electrode configuration 1 (table 3). These findings are very important, because they show that also volumes not directly covered by electrode units are desalinated. This gives some freedom when choosing placement of the electrodes.

4 Conclusions

It has been shown that electrophoresis might be a suitable method to extract salts from a salt-laden substrate. A suitable contact material such as a mixture of calcite/cellulose better protects the masonry against the acidic environment formed at the anode. The extraction rate may vary significantly, depending on the type of salt, the type of substrate, and the type of contact material between the electrodes. Extraction percentages between 20% and 60% were found. This can be obtained in ideal circumstances by which electrodes are positioned at opposite sides of a relatively thin salt laden substrate. Up-scaling to real masonry might prove to be problematic, since real walls are significantly more massive. As a consequence, larger electric tension and more time would be necessary to obtain similar extraction rates.

A possibility to obtain more easily an efficient salt extraction would be the application of electrodes on one side of the masonry. It has been shown that it is possible to perform an efficient extraction by placing electrodes on one side of the masonry. It is not necessary to cover the entire wall with electrodes. A continuous layer of contact material (a wet mixture of cellulose fiber and calcite) that may be 'sprayed' over the wall surface, combined with electrodes covering only part of the wall surface, might be enough for an electrophoresis. Although successfully tested out a wall section of 14 cm thickness [7], it is expected that such desalination will not always be effective in the entire depth of the wall. Most probably the depth of desalination will be similar to the average distance between the positive and negative electrodes, even though this still has to be confirmed through experiments.

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