

## Numerical Modelling of Electrophoresis Applied to Restoration of Archaeological Organic Materials

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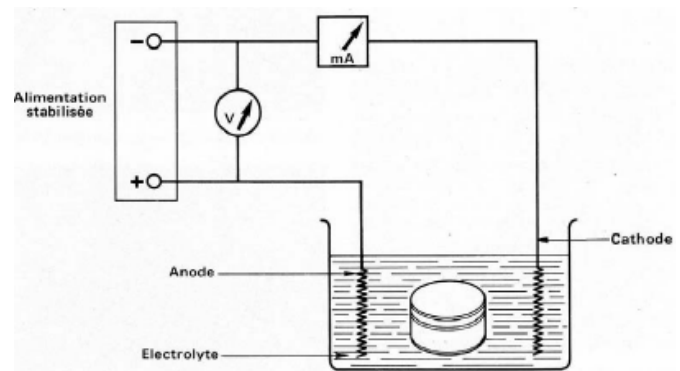
**Abstract:** Restoration of archaeological materials coming from oceans is a major activity of Arc' Antique. Organic materials such as wood, tissues, leathers, papers or ceramics found in sea water are always impregnated of salts. Moreover they are often covered with concretions (carbonates) and contain some salts (ferric, chlorides...) making the restoration particularly difficult. Different techniques were developed in the past decades to get rid of concretions and salt before stabilization of archaeological objects (impregnation process of woods for example). Rinsing such archaeological objects with pure water to extract the salts is too long a process. So electrophoresis was used to improve the salt extraction in the past decades. The objective of this study is the evaluation of the numerical modelling to help improve the electrophoresis process.

**Keywords:** Archaeological materials, Modelling, Restoration Electrophoresis.

### 1. Introduction

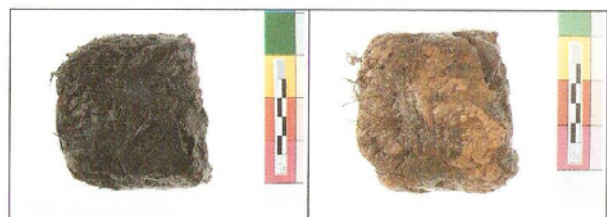
When any object falls at sea, diffusion immediately fills the pores with the salts found in its close environment. When this object is withdrawn from the archaeological site a long time after the shipwreck, it becomes a very fragile historical object to be restored with precaution and in an economic way before exposing it in a museum. Each year, many archaeological organic objects are found on wreck sites. They are often covered with concretions made of salts or metallic compounds (iron sulphides and oxides coming from the close metal parts) but also of carbonates coming from marine organisms. In presence of water or moisture these salts degrade the organic materials very quickly. It is thus necessary to extract the greatest possible quantity of salts before initiating any process of draining and conservation.

As water preserves mainly the cellulose of the degraded wood, water content must be withdrawn slowly to avoid the collapse of wall cells. During the drying process, salts concentrated on the material surface crystallize. To carry out desalination, one generally proceeds to a time consuming series of rinsing in distilled water.



**Figure 1:** Schematic diagram of a electrophoresis treatment [1]

Salts dissolve according to their solubility and the gradient of concentration between material and bath. Thus the rinsing process must be interrupted frequently to change the bath, which lengthens the treatment duration. Moreover, some poorly soluble salts such as iron oxides cannot be extracted in a satisfactory way. This simple process can be accelerated by applying an electric field. Thus electrophoresis was used successfully by Arc' Antique. See for example the valet in figure 2 [2].

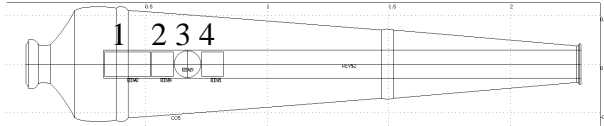


**Figure 2:** Hermione's valet before (left), and after one month electrophoresis (right) [3]. Copyright Arc' Antique - Aubert

### 2. Objectives of the study

The electrophoresis process was used until there in an empirical way. As the treatment usually lasted several weeks or months, its optimization is necessary to gain both duration and cost of treatment. This is the main objective of the modelling. The numerical modelling of electrophoresis process was tested to get a better

understanding of the phenomena and to reduce the processing time of the archaeological objects. We illustrate here the electrophoresis process thanks to the valets shown in figure 2. This valet comes from the French historical ship Hermione wrecked in 1779. As seen in figure 3, the gun was successively charged by the mouth with a powder charge named “gargousse” (1), a bobbin made of hemp threads named “valet” (2), a cannonball (3) and a last valet (4). The two valets were placed in this way to protect both powder and ball from moisture.

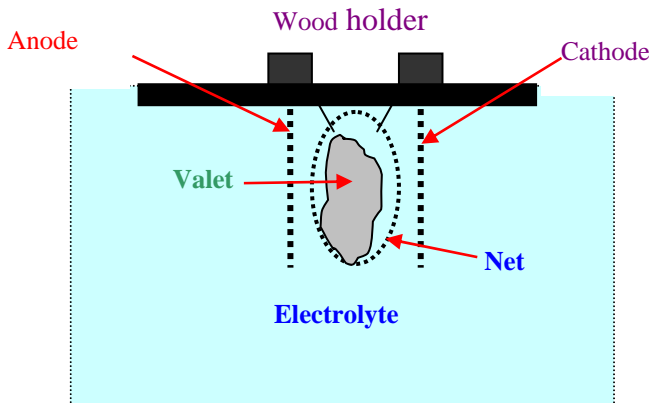


**Figure 3:** Hermione gun cross section  
1=gargousse (powder), 2 and 4=valets, 3=ball

### 3. The electrophoresis process of Arc'Antique

This technique was initiated in 1987 by the EDF Valectra laboratory for the cleaning of the objects found in the Titanic. Thereafter, some studies were made in a more or less empirical way to improve the process [1]. The electrolyte used for this treatment is an aqueous mixture containing 1%  $\text{KNO}_3$  mass. This electrolyte was optimised and selected for its good conductivity ( $0,014 \text{ S.m}^{-1}$ ) [3].

Different electrodes in titanium, graphite, nickel, stainless steel and platinum were successively tested. Finally for sake of simplicity and economic purposes, cheap deployed stainless steel sheets were used as cathode and anode. During the electrophoresis of an organic object, it is necessary to control the pH which must remain neutral since organic objects are degraded in acid or basic media. The experimental apparatus shown in Figure 4 appears as very simple, liable and cheap. The fragile valet is placed in a net to be hold in the electrolyte, so it can be handled easily.



**Figure 4:** The experimental apparatus

## 4. Mass transport in a porous body

### 4.1. Convection Diffusion application

Models of diffusion can be used to calculate the time necessary to extract by rinsing a given salt from a porous object. Since it is not possible to carry out a sample from archaeological objects to measure their salt concentration, it is also necessary to estimate it a priori, ad this is possible thanks to numerical calculation. In both cases we used the Convection Diffusion application of COMSOL [4, 5]:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = R_i - u \nabla \cdot c_i \quad (1)$$

where  $C_i$  is the concentration,  $D_i$  the related coefficient of diffusion of  $i$  species.

The organic objects being frequently porous, we used the usual models of porosity taking account of the tortuosity and the contraction of the pores.

### 4.2 Nernst-Planck application

When applying an electric field thanks to two electrodes immersed in the solution the ionic species  $i$  of charge  $z_i$  and concentration  $c_i$  migrate with a ionic mobility  $u_{mi}$  according to the following expression:

$$N_i = -D_i \nabla c_i - z_i u_{mi} F c_i \nabla V + c_i u \quad (2)$$

The electro neutrality condition is:

$$\sum z_i c_i = 0 \quad (3)$$

Combining equations and gives the Nernst-Planck equation:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i - z_i u_{mi} F c_i \nabla V + c_i u) = R_i \quad (4)$$

The COMSOL Nernst-Planck application (with electro neutrality) describes perfectly the mass transport by diffusion, migration and electro migration of the electrolysis process. It was used in a straightforward way.

## 5. Numerical model

Numerous assumptions were made to model the valet. First the quasi cylindrical valet was modelled in 2D thanks to its axial symmetry. This simplification gives true 3D results, though the computation uses only two dimensions.

We also assumed that the electrolyte support was not consumed.

We could not analyze the valet composition at first since one cannot take a sample from the valet. Then the initial conditions of concentration have to be estimated. Several types of ions are present in the archaeological object resulting from its environment, like the chloride ions coming from sea water and ferrous-ferric ions coming from the corrosion of the metal objects found in its vicinity. Since the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio was unknown, we assumed for sake of simplicity that only  $\text{Fe}^{2+}$  ions are present within the object. However it would be straightforward to take account of  $\text{Fe}^{3+}$  concentration when it is known.

The archaeological organic objects usually restored are more or less sintered. The concretion distribution around the object results from diffusion of ionic species present in the marine environment and its position in the wrecked ship. Thus the initial conditions of an archaeological problem are defined by:

- presence or absence of metal pieces in the vicinity likely to deliver metal ions,
- salt composition of the local submarine environment in which it was immersed,
- time spent in the sea,
- agitation of the marine environment.

One of the major issues of the electrophoresis process is the evaluation of the nature and the quantity of concretions present in the valet to be treated, i.e. the initial concentrations of salt and oxides of the treated system. It is indeed unthinkable to sacrifice an archaeological object which has a significant historical importance. Then it is impossible to cut the sample to see the distribution of concretions and one cannot thus make preliminary analyses to measure their initial composition.

This problem was solved by computing the effect of diffusion to evaluate the missing data. It was found that  $\text{Fe}^{2+}$  concentration is more symmetrical in the left valet than the right one. However the mean concentrations are similar for both valets and this value was used as initial  $\text{Fe}^{2+}$  concentration condition for the modelling of each valet. It must be emphasized that the initial salt concentration in the valet is of great importance for the choice of cell voltage, process duration, and finally the restoration cost. The method cannot be validated actually without precise experimental tests. It appears evident that the subsequent step will be the calibration of diffusion prediction using an archaeological piece (of wood for example) without any archaeological significance which could be cut and precisely analysed.

For the same reasons, porosity is an important parameter required to make a suitable modelling of the electrophoresis process. It is particularly true for the valet which was made of

hemp threads rolled as perpendicularly crossed tablecloths to make a spherical bobbin. One can imagine that such a thread structure has an anisotropic porosity. Moreover the presence of concretions blocking up the pores gradually is another problem related to the porosity of the system which is generally not known.

Other parameters related to porosity, like the tortuosity and the contraction of the pores are required for calculations. As one cannot get these parameters from literature or direct analyses on archaeological material, these parameters were all estimated. For example a 74 % porosity was assumed for the Hermione valet from similarity with archaeological tissues.

The diffusion coefficients of the ionic species present in  $\text{KNO}_3$  electrolyte are measured at infinite dilution. These coefficients are obviously criticisable since the simulation of diffusion proves that after two centuries the concentration in the valet was far from diluted. In conclusion, the estimation at first of all the parameters involved in the modelling is a key issue which cannot be solved for an unknown material.

## 5.1 DC Boundary conditions

For DC application, the tank walls are assumed insulated. At both electrodes, the electrochemical reactions are assumed very fast, and then we applied constant potentials at electrodes:

$$V = V_0 \quad (3.6)$$

The following potentials were measured with an SSE (reference electrode): 1.1 V at anode and -1.8 V at cathode. These values were introduced as Dirichlet condition at electrodes.

Since the object is porous, the solution of electrolyte fills its pores thus the current flows through its pores. The electric conductivity took account of its porosity and tortuosity.

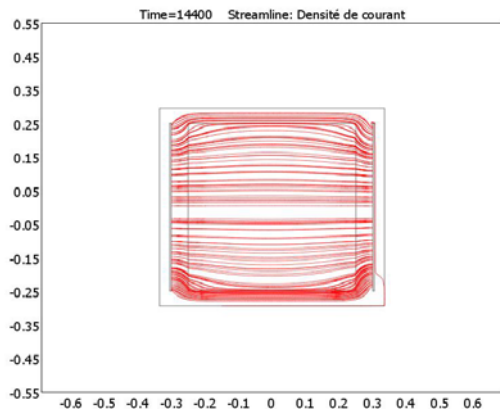
## 5.2 DC Boundary conditions

For Nernst-Planck application, the  $\text{KNO}_3$  concentration was constant since the electrolyte support was assumed not to be being consumed. The tank walls do not participate to chemical or electrochemical reaction. Thus a null normal flow for each ionic species present in solution was imposed at wall. To simplify our system, we also assumed that due to the choice of working potentials there was no release of  $\text{H}^+$  at anode or  $\text{OH}^-$  at cathode. We also supposed that all the  $\text{Fe}^{2+}$  ions extracted from the object were deposited on cathode after migration. Therefore cathode is regarded as a well of  $\text{Fe}^{2+}$  ions with a limit current

condition, and then null concentration  $\text{Fe}^{2+}$  was put on the cathode.

## 6. Main results and discussion

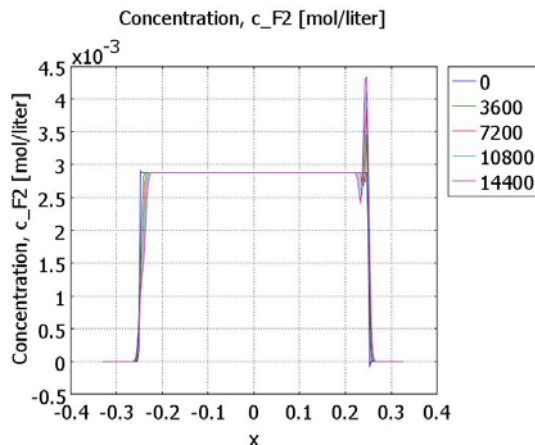
Figure 4 shows the current density stream lines which flow through the whole object whose porosity was assumed homogeneous. The valet has actually an extremely heterogeneous and asymmetrical porosity due to its structure and presence of concretions and is probably more complex. Further models will have to take account of conducting concretions and anisotropic porosity.



**Figure 4:** current density lines crossing the object

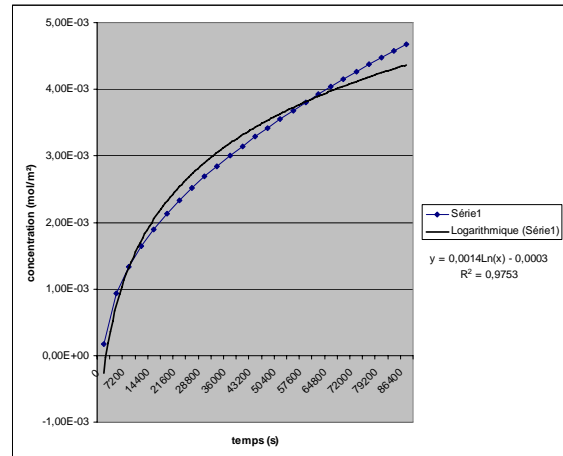
At the beginning of the treatment, the  $\text{Fe}^{2+}$  concentration ions is assumed constant in the object and is null in the electrolyte.

Figure 5 illustrates the effect of electrophoresis at first times, namely the migration of  $\text{Fe}^{2+}$  cations towards the cathode. Then the  $\text{Fe}^{2+}$  concentration increases with time in the cathode side of electrolyte and decreases gradually in the anode side of the object.  $\text{Fe}^{2+}$  ions lost in the objet (left) are found in the electrolyte (right). A zone of depletion appears at the right end of object but its central part remains at the initial concentration.



**Figure 5:** Successive spatial distributions of  $\text{Fe}^{2+}$  in the valet

Then it is clear that a thick object will require a larger time to be restored than a thin one.



**Figure 6:**  $\text{Fe}^{2+}$  concentration in solution versus time (in seconds)

According to figure 6, the concentration in solution of  $\text{Fe}^{2+}$  ions extracted from the valet increases rapidly in a quasi logarithmic way.

Though the model was not yet properly fitted this trend compares favourably with the measurements of concentration in solution.

In conclusion the major issue to model the electrophoresis process is related to the lack of numerous data: initial salt concentrations in the archaeological material, diffusion coefficient of all the ions found in electrolyte, presence of concretions, values of porosity, tortuosity and restriction. Some process parameters must be also studied namely distance electrode-object, frequency of electrolyte renewal, volume of electrolyte ... A sensibility analysis could be of some help to improve the quality of prediction.

## 7. Conclusions

The use of COMSOL Diffusion and Nernst-Planck applications gave first promising results for the modelling of the electrophoresis process. The simulation of valet treatment has shown the advantages and limitations of the restoration process for large pieces. It appeared that electrophoresis is ideal to restore very thin objects. The lack of data for archaeological objects of interest is a true limitation. Then the method has to be calibrated precisely by use of sacrificial pieces of wood for example. This study provides interesting directions for future modelling of the electrophoresis for organic archaeological objects to evaluate the efficiency of this technique.

## 8. References

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