

Use of electrochemical techniques for the conservation of metal artefacts: a review

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Abstract Electrochemical techniques like mechanical and chemical ones should be among the panoply of techniques conservators normally use when they conserve metal artefacts. Often though, they are discarded because they are considered as too complicated and dangerous. As a consequence, not much development in the use of these techniques in conservation was observed before the 1990s when their application to marine artefacts once again drew the attention of conservation professionals. More recently, the latter have recognised the importance of these techniques in the understanding of corrosion processes as well as their monitoring and in the solving of specific conservation issues. Furthermore, instruments that were previously only used by corrosion scientists are today entering the conservation field. Portable tools have even been designed so that treatments can be carried out in situ. The current trend is to cluster electrochemical and analytical techniques in parallel in order to fully understand the behaviour of metal artefacts when conserved.

Keywords Conservation · Storage · Cleaning · Stabilisation · Electrochemical techniques

Introduction

Electrochemical techniques are extensively used by scientists working in corrosion science to study corrosion

mechanisms, corrosion resistance of materials in specific environments and protection systems [1].

The examination and conservation of archaeological and historic metal artefacts is another field where such techniques have found many applications: first, to analyse metal artefacts. Indeed corrosion potential (E_{corr}) vs time or voltammetric curves can be utilised to analyse qualitatively or quantitatively metal artefacts [2, 3]. Secondly, corrosion mechanisms affecting archaeological and historic metal artefacts before or during their treatment can be more easily understood. The in situ monitoring of marine metal artefacts [4], the corrosion study of iron artefacts associated to waterlogged organic materials when consolidated in polyethylene glycol solutions [5] and the study of pitting corrosion or/and cathodic corrosion on marine aircrafts remains made of aluminium alloys when stabilised¹ in aqueous solutions [6, 7] are good examples of such an application. Finally, conservation professionals working on heavily chlorinated artefacts (from marine or terrestrial sites) employ them either to monitor the storage of the artefacts in solution [8] or more frequently to clean, stabilise and protect them [9]. Other typical applications are the cleaning of silver tarnish [10], the consolidation of heavily corroded lead objects previously stored in wooden cabinets (evolving acetic acid) [11] and the protection of metal artefacts [12, 13].

The aim of this paper is to present the approach followed by conservation professionals when applying electrochemical techniques for the conservation of metal artefacts. Their advantages compared to other techniques as well as their limits will be discussed. Some interesting perspectives will be presented too.

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¹ Extraction of aggressive species such as chlorides that provoke active corrosion.

Theoretical background required

From the end of the nineteenth century to the beginning of the 1980s, electrochemical techniques were used without any control of the potential of the metal artefact considered. Rathgen [14] and his followers (Fink C, Eldridge C.H, Efficient method for restoration of antique bronzes badly corroded or crusted over. Unpublished typescript. Walters Art Gallery, 1923) till Plenderleith [15] and Hamilton [16] applied constant external currents to stabilise active bronze artefacts. North working on marine artefacts preferred to apply constant voltages [17]. As a consequence, reactions developing on the metal surface were not monitored, and often, some transformation of the natural patina were observed but not entirely understood.

Only in the late 1980s, the use of the potential of the object to monitor its behaviour in solution or define the proper treatment conditions was first mentioned [18]. The Valectra division of Electricité de France played here a major role, and this contribution has marked the entry of electrochemistry in conservation science.

Since conservators use electrochemical processes both during the immersion and the polarisation of metal artefacts in solution, we will review the meaning of the potential taken by a metal artefact when immersed in a solution (corrosion potential, E_{corr}) as well as the consequences on the metal surface of the modification of this potential when polarising it cathodically or anodically.

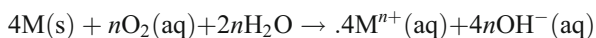
Behaviour of metal artefacts during immersion

Meaning and measurement of E_{corr}

Most conservation professionals have a basic and theoretical knowledge on the electrochemical behaviour of metals in aqueous solution (Nernst equations, Pourbaix diagrams [19]). Still, they usually ignore how the corrosion potential E_{corr} (or open circuit potential or rest potential) can be used to determine this behaviour in the solution chosen. Traditionally, the electrochemical reactions of metals in aerated aqueous solutions can be divided into the oxidation and reduction half reactions taking place at the anodic and cathodic sites such as:

- Dissolution of the metal (*oxidation*)
 $\text{M(s)} \rightarrow \text{M}^{n+}(\text{aq}) + n\text{e}^-$ resulting in the anodic current I_a
- Reduction of the dissolved oxygen $\text{O}_2(\text{aq})$ in the solution:
 $\text{O}_2(\text{aq}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ resulting in the cathodic current I_c

At E_{corr} , the system is at steady state ($I_a + I_c = 0$), which corresponds to the following equation:



In reality, several oxidation and reduction processes can occur simultaneously, and E_{corr} reflects all the half reactions (anodic ($I_a > 0$) and cathodic ($I_c < 0$)) taking place at the same time on the metal without an external current.

E_{corr} is measured with a multimeter vs a reference electrode (RE). Different reference electrodes may be found on the market but the more common one is the Ag–AgCl reference electrode. Its potential vs the standard hydrogen electrode (SHE) is around 0.2 V/SHE.

The exact value of E_{corr} is not so important. Instead, it is essential to understand the influence of some parameters on this value. The actual corrosion or passivation (formation of a protective corrosion layer) of metals can be determined from E_{corr} vs time plots: an increase on a bare metal corresponds to a passivation phenomenon and a decrease to a corrosion process (see Fig. 1).

These phenomena will obviously depend on the volume of solution used especially when corrosion occurs. The presence of an oxide layer or any corrosion layer will modify the value of E_{corr} compared to the one read for bare metals.

Pourbaix diagrams

The pH of the solution in which the metal is immersed is another important parameter affecting E_{corr} . Pourbaix E/pH diagrams can be used to predict the behaviour of the metal (either immunity (no corrosion), corrosion or passivation) [19]. Since the metal considered is rarely pure and the potential is not measured at standard conditions, such diagrams have to be used with care, and E_{corr} vs time plots are still needed to verify the actual behaviour of the metal in the solution considered.

For obvious reasons, conservation professionals choose a solution with a pH favouring the passivation of the metal surface. For iron, passive conditions are obtained in alkaline solutions (see Fig. 2): formation of $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ within the field of stability of the aqueous media. Since KOH or NaOH have strong wetting properties and OH^- anions are easy to remove during the rinsing process, these solutions are commonly used for storage and

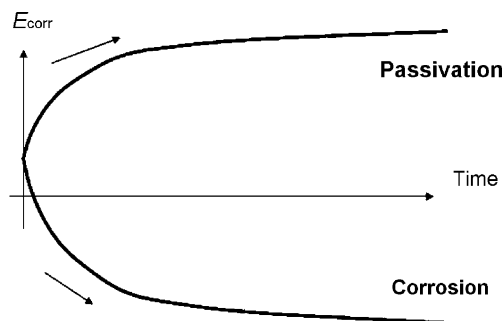
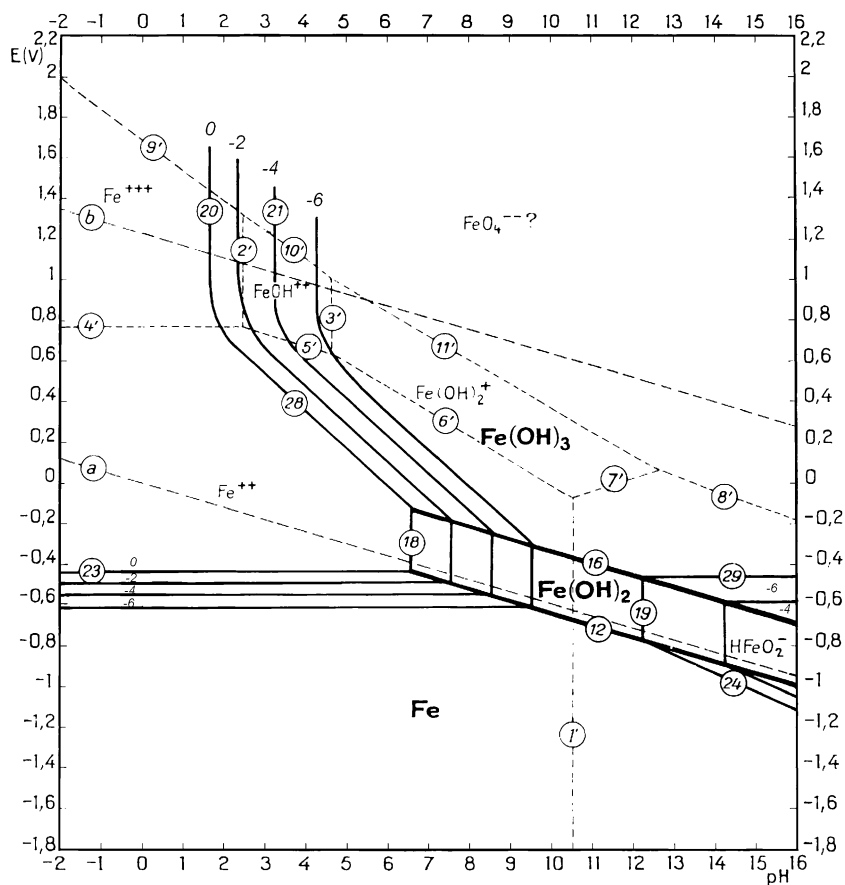


Fig. 1 Electrochemical behaviour of a metal artefact in solution through the monitoring of E_{corr} vs time

Fig. 2 Pourbaix E (V/SHE)–pH diagram of Fe at 25 °C. Diagonals (a) and (b) correspond to the lower and upper limit of stability of the aqueous media [19]



stabilisation treatment of iron artefacts [9]. Passive conditions for copper are obtained in slightly alkaline solutions. Due to the transformation of active copper chlorides to stable carbonate compounds, buffered sodium sesquicarbonate $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ (pH=10–11) is traditionally used to store and stabilise copper-based artefact [20, 21].

Behaviour of metal artefacts when polarised

The kinetic of electrochemical reactions is not considered in Pourbaix diagrams. Reactions that should develop at a certain potential might be so slow that nothing visible is actually occurring. To have a better idea on the kinetics of electrochemical reactions, it is necessary to plot $I=f(E)$ curves. Voltammetric studies consist of scanning the potential of the metal from E_{corr} to a cathodic or anodic potential chosen by the user.

The potentiostat is a piece of equipment specifically designed to achieve this work. It is a sophisticated power supply with three terminals connected to a three-electrode cell device controlled by a pilot connected to a PC (see Fig. 3). The three electrodes are the following:

- Working electrode (WE): metal considered.
- Counter electrode (CE): usually a platinum grid.

- RE: the reference electrode is maintained continuously in the electrolyte to give a direct measurement of the potential applied to the metal considered (WE).

Before studying the electrolytic behaviour of a metal in a specific electrolyte, we first check with a platinum WE that the latter is not electrochemically reactive. The next step is to determine the potentials of the reactions to provoke. To prevent any damage on real artefacts, artificial metal coupons representative of the alteration of real artefacts

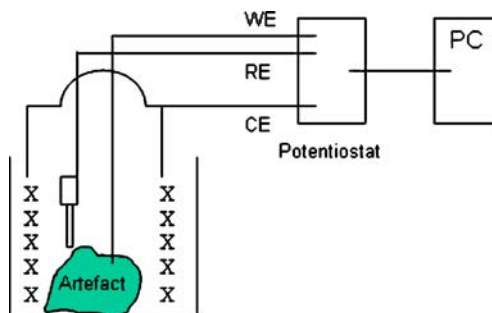


Fig. 3 Electrochemical device using a potentiostat to polarise a metal artefact

are normally used. In conservation, we are often interested in the cathodic polarisation of metal artefact. Therefore, cathodic reactions developed on the metal in the electrolyte chosen are studied first. In case anodic reactions have to be studied, a new artificial coupon has to be considered, and the same methodology as before is applied.

Reading $I=f(E)$ plots

Starting from E_{corr} , reduction reactions are favoured if the potential is decreased in the cathodic direction (see Fig. 4). The plateau of current corresponding to the reduction of oxygen dissolved in solution is observed first. It is followed by one or several peak(s) starting at E_{cp} (cp refers to cathodic peak) that correspond(s) to the reduction of the metallic species M^{n+} or others. Finally, the important wave corresponds to the evolution of hydrogen, starting at E_{H_2} . Anodic polarisation favours oxidation reactions: oxidation of the metal before the decomposition of the aqueous media (oxygen bubbling).

Using $I=f(E)$ plots

In conservation, different processes are artificially provoked when polarising metal artefacts. Mechanical cleaning of marine crusts is possible through H_2 evolution at the interface between the conductive corrosion layer of the metal surface and the concretion. Stabilisation of active metal artefacts is achieved through the reduction of corrosion products that favour the extraction of aggressive species (such as chlorides). The protection of metal artefact is obtained by the formation of passive layers (mostly metal oxides).

If the parameters are not chosen carefully (through $I=f(E)$ plots), side effects may occur (extensive hydrogen bubbling under cathodic polarisation might cause local embrittlement, and inadequate reduction of corrosion products change irreversibly the appearance of the metal

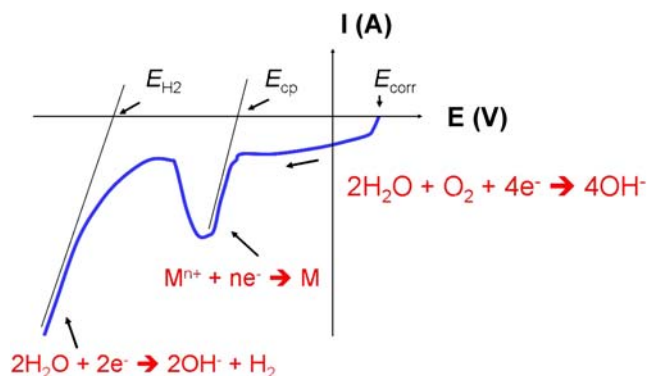


Fig. 4 Voltammetric plot in the cathodic field and in neutral solution from E_{corr} to the evolution of hydrogen

Table 1 Conditions for the electrochemical treatment of iron- and copper-based artefacts [20, 22]

Support	Purpose	Treatment conditions (solution and potential applied)
Iron	Cleaning	1% w/v NaOH or KOH solution, $E_c = -0.85$ V/SHE
	Stabilisation	Same solutions, $E_c = -0.75$ to -0.8 V/SHE
Copper	Stabilisation	1% to 5% w/v sodium sesquicarbonate, $E_c = -0.1$ to 0 V/SHE

surface). The potentials applied (E_c (for cathodic) and E_a (for anodic)) are usually corresponding to the maximum of the reduction (E_{pmaxc}) or oxidation (E_{pmaxa}) peaks. The values are those given in the literature. Table 1 gives examples of potentials actually used by conservation professionals to treat iron and copper-based artefacts [20, 22].

To apply these values, conservators do not normally use a potentiostat that are not available in conservation laboratories but more commonly power supplies (having 2 terminals only (+ and -)). Still, the potentials of the objects are established and regularly monitored with reference electrodes (see Fig. 5).

Platinum is never used as a counter electrode (anode) when treating cathodically artefacts. Another less expensive electrode but still electrochemically inactive is considered: stainless steel for iron artefacts in KOH solutions and for copper alloys in sodium sesquicarbonate solutions and lead plates for lead artefacts in neutral sodium sulphate solution [9–11].

To keep constant the potential applied to the metal artefact in order to provoke the reduction of specific corrosion products or the oxidation of metallic species on the metal surface requires some attention. If not monitored, this potential will shift towards more negative (in case of cathodic polarisation) or more positive (in case of anodic polarisation) values. It will eventually provoke either the reduction of all existing corrosion products and the decomposition of the solution in hydrogen during the cathodic polarisation or the decomposition of the solution in oxygen

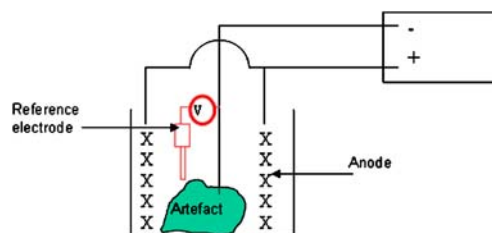


Fig. 5 Electrochemical device using a power supply to polarise an artefact. The reference electrode is added to the circuit only to establish and regularly monitor the potential of the metal artefact



Fig. 6 Monitoring of E_{corr} vs time on a swivel gun recovered in Maltese waters and stored in 1% w/v NaOH solution. The size of the tank was too big, and containers filled with water were placed in it to limit the volume of the solution to the minimum (credit D. Vella)

during the anodic polarisation. Therefore, the use of a potentiostat is preferred on small and fragile artefacts where it is often difficult to avoid these side effects. A way to prevent definitely the decomposition of the solution in hydrogen and oxygen during the polarisation of the artefact is to use pulsed currents ($i=i_1$ during $t=t_{\text{on}}$, $i=0$ during $t=t_{\text{off}}$) and limit potential ($E_{\text{limc}} < E$ in the cathodic field

and $E < E_{\text{lima}}$ in the anodic one). This approach was successfully developed for the stabilisation of marine iron artefacts where the extraction ratio $Q_{\text{Cl}}/Q_{\text{total}}$ increased from 0.17 in potentiostatic mode to 0.49 in pulsating mode with an optimised constant cathodic current $i_c = -300 \mu\text{A}$ during $t_{\text{on}} = 60 \text{ s}$ ($i=0$ during $t_{\text{off}} = 30 \text{ s}$) and $E_{\text{limc}} = -0.74 \text{ V/SHE}$ [23].

Applications

Monitoring of artefacts during storage and immersion in aqueous solutions

When recovered from the sea, marine metal artefacts are often cleaned mechanically to remove their crust and reveal their metal surface. Once exposed to the atmosphere, the artefact contaminated with chlorides becomes active, and the flaking of the original surface is usually observed. This is particularly true for iron-based artefacts [22]. Therefore, these artefacts are immediately stored in an alkaline solution (1% w/v KOH or NaOH giving a pH=13). Figure 6 illustrates these storage conditions in the case of a breach loading swivel gun recovered from the Maltese waters in June 2000.

During the storage, we usually monitor both the potential of the artefact and the concentration of chlorides extracted

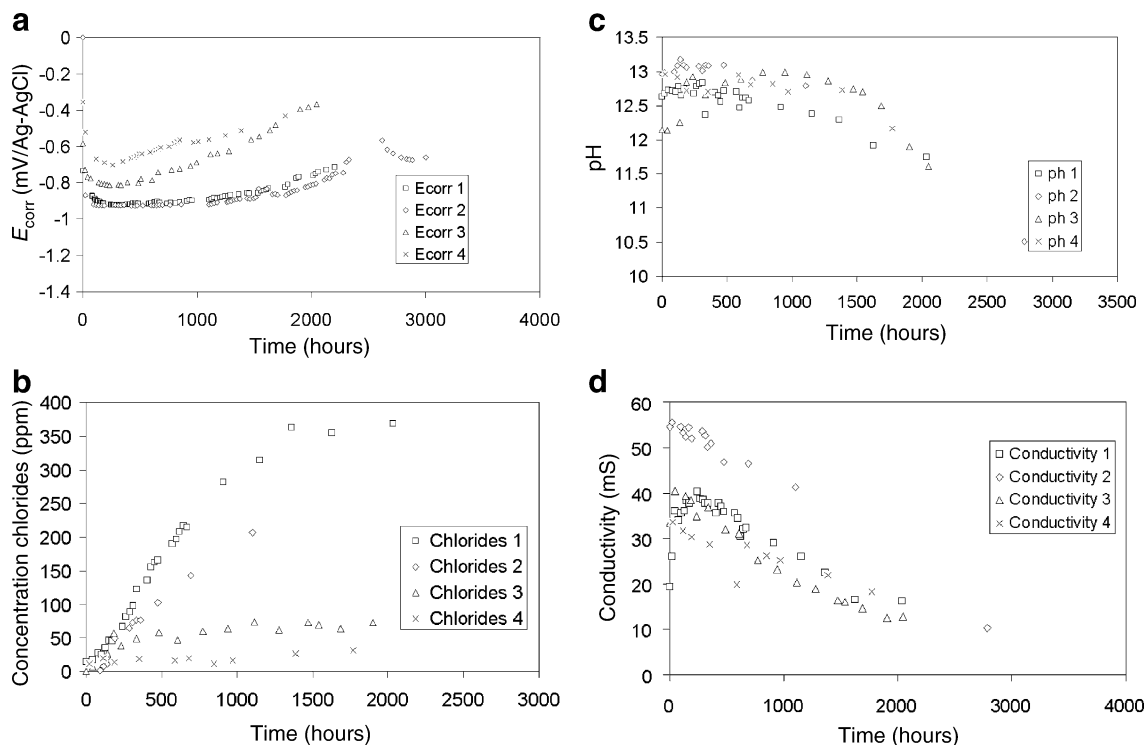


Fig. 7 a–d E_{corr} (vs Ag–AgCl), C_{Cl^-} , pH and conductivity of the solution vs time plots during the storage/stabilisation of the swivel gun presented in Fig. 6. (squares first bath, diamonds second bath, triangles third bath and multiplication signs fourth bath)

(see Fig. 7a and b). The change of solution is decided when the concentration of chlorides extracted has reached a maximum in the solution considered. Today, other parameters are monitored too such as the pH (see Fig. 7c) and the conductivity (see Fig. 7d) of the solutions to have a full control on the artefact and the electrolyte in which it is immersed.

We clearly observe on E_{corr} vs time plots that first, the potentials decrease, remain stable and re-increase steadily. The preliminary decrease of the potential is due to the reaction of the solution with the existing corrosion layer [8]. Once the solution has reached the metal surface, the normal passivation phenomenon (increase of the potential) is observed, and as expected, the re-increase of potential is faster during the third and the fourth immersion steps.

Chlorides on iron-based artefacts are concentrated at the interface between the remaining metal and the corrosion layers [24]. As shown on Fig. 7b, the extraction of chlorides proceeds during the transformation of the whole corrosion layer by the solution. That means basically during the first two immersions. Interestingly, the pH and the conductivity of the solution decrease during the immersion. This change in the chemistry of the solution is still not fully understood.

Electrolytic cleaning of tarnished historical silver artefacts

Silver artefacts get tarnished when they are exposed to sulphur atmospheres or chlorinated media (such as human sweat) [10]. Different techniques (mechanical, chemical and electrolytic) have been applied to clean tarnished historical artefacts. Of them all, the cathodic polarisation is the less aggressive.

As indicated in Fig. 8 showing the cleaning of a silvered brass vase in 1% w/v sodium sesquicarbonate, the potential

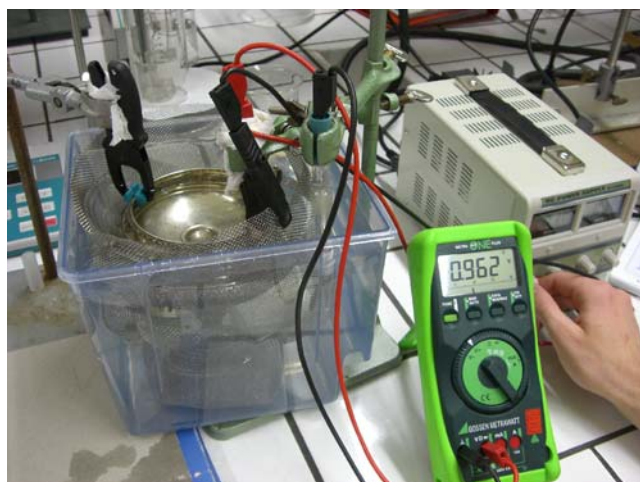


Fig. 8 Cleaning of a tarnished silvered brass vase by cathodic reduction at -0.75 V/SHE in 1% w/v sodium sesquicarbonate

of the reduction is around -0.75 V/SHE (corresponding to E_{pmaxc} of the peak of reduction of Ag_2S).

At this potential, AgCl is reduced too (E_{pmaxc} around 0.15 V/SHE). The reduction process can be monitored by chronoamperometry ($I=f(t)$ plots) as represented in Fig. 9.

When cleaning silver tarnish on a metal artefact, one has to check whether the artefact is plain silver or only silvered. In the latter case, the supporting material is often copper-based. If the silver layer on top got damaged, copper oxides and sulphides have formed [10, 25]. Depending on the extent of this process, it might be that during the cathodic polarisation, stains due to reduced copper are observed. Chelating agents such as EDTA tetrasodium are commonly used as a pretreatment of such artefacts [26].

A similar attention is required when cleaning silver tarnish on gilt silver objects. If reduced in a same way as before, the surface of the gold will be covered with reduced Ag. For that reason, a second electrolytic step is required to dissolve the reduced Ag in Ag^+ . This time, the artefact is polarised anodically in a new 1% w/v sodium sesquicarbonate solution at the potential corresponding to the maximal oxidation of Ag in Ag^+ . Such an approach (preliminary cathodic polarisation followed by an anodic polarisation) has been used to clean the gilt silver plates of the shrine of St Sigismund's children (St Maurice Abbaye-CH) at the Laboratory of the Museum of Art and History (Geneva, CH) [27].

After the cleaning process, the artefact is often quite dull, and a slight polishing with cotton is needed to recover the initial shine.

Stabilisation of lead artefacts altered by volatile organic compounds in neutral solution

Lead artefacts are often found in archives (seals and tokens) and are usually covered with thick corrosion layers made of

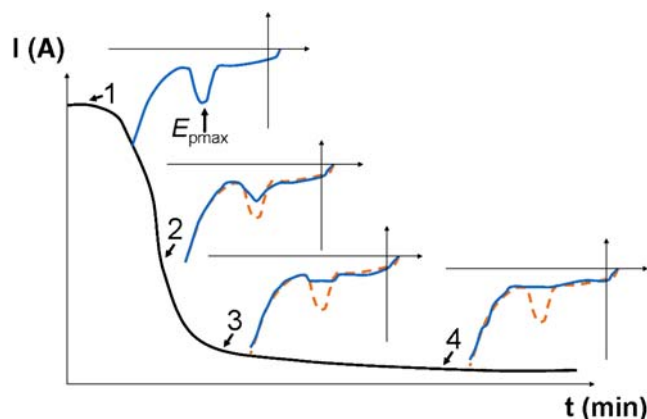


Fig. 9 Monitoring of the reduction process on tarnished silver through the measurement of the current vs time at $E_{\text{pmaxc}} = -0.75$ V/SHE. The decrease of the current at the peak corresponds to the progressive disappearance of Ag_2S as indicated by steps 1 to 4

powdery lead carbonate (see Fig. 10). This alteration has been thoroughly described in the literature and is due to the evolution of volatile organic compounds (VOC) in the wooden cabinets where the artefacts are stored [28].

Consolidative reduction is one of the most successful treatments for these artefacts [11]. Different electrolytes have been tested but neutral sodium sulphate is particularly adapted to lead objects associated to organic materials (seals attached to parchments). In Na_2SO_4 0.5 M solution, the cathodic potential to apply is -0.65 V/SHE. The reduction of lead corrosion products is once again monitored by chronoamperometry ($I=f(t)$ plots) as shown in Fig. 11. Four steps are observed. The current first increases to reduce lead carbonates (step 1) but decreases abruptly afterwards (step 2) before reaching quite low values. At step 3 the surface of the artefacts seems to be metallic but corrosion products are still present underneath. They are fully reduced at step 4. Since steps 3 and 4 are difficult to differentiate from $I=f(t)$ curves, we usually plot $\log(I)$ vs time.

It is possible today to treat composite artefacts like lead seals represented in Fig. 10 by protecting fully the parchment in a thermally sealed polyethylene film and the threads with a thick layer of cyclododecane (CDD).



Fig. 10 Lead seal still attached to a parchment (partly visible on the top of the photograph) with died silk threads and covered with powdery lead carbonate indicating an exposure of the artefact to VOC (credit Arc'Antique)

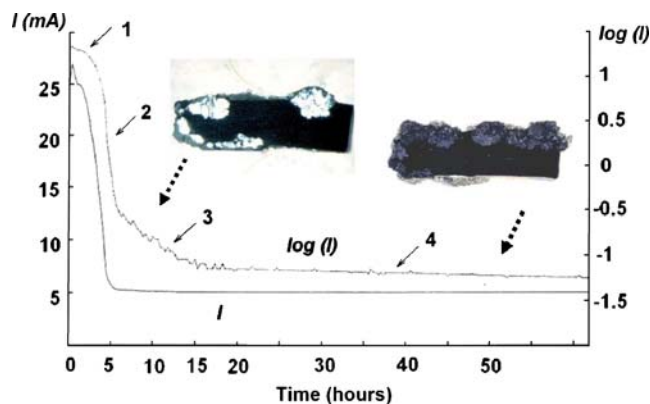


Fig. 11 Chronoamperometry plot showing the progressive reduction of corrosion products on cross sections of lead weights polarised at -0.65 V/SHE in 0.5 M sodium sulphate. At step 3, the reduction is still partial, while at step 4, it is complete (credit Arc'Antique)

Figure 12 shows the consolidative reduction of such an object in progress.

New perspectives

The study of the impact of the environment on metal artefacts is essential if we want to prevent their corrosion and limit to the minimum any conservation intervention. The monitoring of the tarnishing on silver coupons in showcases in museums [29] or the assessment of the compatibility of stainless steel in sealing compounds used as reinforcing structures in historic buildings [30] are two examples of the application of electrochemical techniques in preventive conservation strategies.



Fig. 12 Consolidative reduction of an altered lead seal still attached to its parchment by cathodic polarisation. The non-immersed parchment is protected in a thermally sealed polyethylene film, while the threads are protected both by a thick layer of CDD and for the outer threads by an extra thermally sealed polyethylene film (credit Arc'Antique)

Electrochemical impedance spectroscopy is traditionally used by corrosion scientists to assess the efficiency of various protection systems (corrosion inhibitors or coatings) on metal surfaces. Some interesting studies have been carried out recently on the protection of metal artefacts during and/or after their treatment [12, 13, 31, 32].

While many artefacts are currently treated using electrochemical techniques, the exact effect of electrochemical processes on artefacts and their corrosion layers is still not fully understood. To have a better idea of the processes involved, we can combine the measurement of electrochemical parameters (E_{corr} vs time, chronoamperometry) to the analysis of metal surfaces using the most up-to-date equipment. Time-resolved X-ray diffraction or X-ray absorption data in a synchrotron beam line have been tested on artificially corroded copper-based coupons while immersed in sodium sesquicarbonate in order to follow up the transformation of the corrosion layers during the stabilisation of active copper-based artefacts [33]. The specifically designed cell device (eCell) used is the same as for the real-time spectroelectrochemical study of the protection of lead artefacts by immersion in sodium carboxylate [34].

Other interesting applications are the use of local electrochemical treatments (cleaning of silver tarnish on composite artefacts that cannot be immersed and local stabilisation of active corrosion) that is still in development and the remote monitoring, via internet, of electrochemical treatments of large marine artefacts on the site of their discovery [35]. During the development of the latter technique, it was found out that due to a better control of all parameters involved, the treatment is carried out in a much safer way.

Conclusion

The use of electrochemical techniques in conservation requires some basic knowledge on electrochemical parameters and processes but more importantly collaboration between end users (conservators) and corrosion scientists. If some techniques can easily be handled by conservators (monitoring of E_{corr} vs time), others can only be developed by specialists knowledgeable in electrochemical processes before being applied on a daily basis by the same end users. Therefore, a multidisciplinary approach of conservation problems and the way to solve them is necessary in order to develop conservation treatments really adapted to each artefact.

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